Inorganic Chemistry

Article

pubs.acs.org/IC

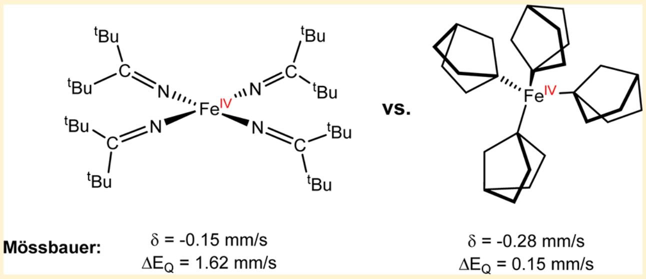
Reactivity and Mössbauer Spectroscopic Characterization of an Fe(IV) Ketimide Complex and Reinvestigation of an Fe(IV) Norbornyl Complex

Richard A. Lewis,[†] Danil E. Smiles,[†] Jonathan M. Darmon,[‡] S. Chantal E. Stieber,[‡] Guang Wu,[†] and Trevor W. Hayton*,[†]

[†]Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States

[‡]Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

Supporting Information



ABSTRACT: Thermolysis of $Fe(N{=}C^tBu_2)_4$ (**1**) for 8 h at 50 °C generates the mixed valent Fe(III)/Fe(II) bimetallic complex $Fe_2(N{=}C^tBu_2)_5$ (**2**) in moderate yield. Also formed in this reaction are *tert*-butyl cyanide, isobutane, and isobutylene, the products of ketimide oxidation by the Fe^{4+} center. Reaction of **1** with 1 equiv of acetylacetone affords the Fe(III) complex, $Fe(N{=}C^tBu_2)_2(acac)$ (**3**), concomitant with formation of bis(*tert*-butyl)ketimine, *tert*-butyl cyanide, isobutane, and isobutylene. In addition, the Mössbauer spectra of **1** and its lower-valent analogues $[Li(12\text{-crown-}4)_2][Fe(N{=}C^tBu_2)_4]$ (**5**) and $[Li(THF)]_2[Fe(N{=}C^tBu_2)_4]$ (**6**) were recorded. We also revisited the chemistry of $Fe(1\text{-norbornyl})_4$ (**4**) to elucidate its solid-state molecular structure and determine its Mössbauer spectrum, for comparison with that recorded for **1**.

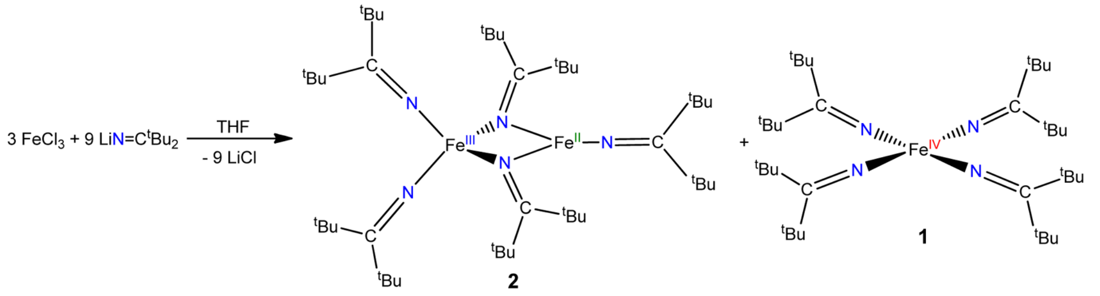
INTRODUCTION

Fe(IV) is both a biologically relevant and synthetically useful oxidation state.[1−5] From a synthetic standpoint, numerous researchers have demonstrated the utility of the $[Fe{=}O]^{2+}$ moiety to effect a variety of epoxidations and aliphatic C−H activations.[1,6−8] For example, Que and co-workers have shown that $[Fe(O)(TMG_2dien)(MeCN)]^{2+}$ (TMG_2dien = 1,1-bis{2-[N^2-(1,1,3,3-tetramethylguanidino)]ethyl}methylamine) can rapidly oxidize 1,4-cyclohexadiene and 9,10-dihydroanthracene,[9] while White and co-workers have used Fe-catalyzed C−H hydroxylation to synthesize several complex natural products.[10−12] Similarly, in the aziridination of alkenes with aryl azides, an Fe(IV) imido, $[Fe{=}NR]^{2+}$, is a proposed intermediate in the catalytic cycle.[13] In a few instances, the Fe(IV) moiety implicated in catalysis has been isolated and structurally characterized;[14−16] however, in many cases these Fe(IV) complexes are far too reactive to isolate,[7,9,17−20] in part because of the highly oxidizing nature of these intermediates.

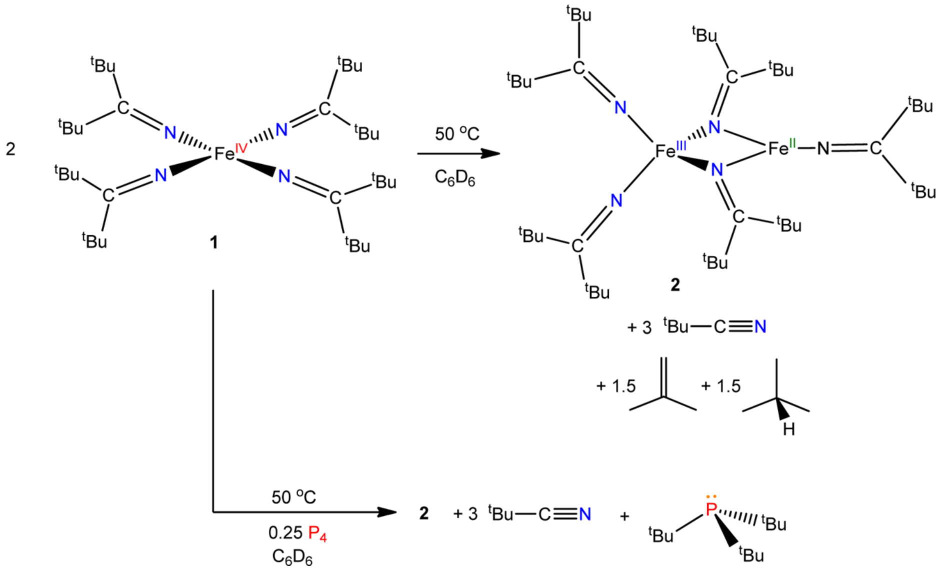
We recently reported the synthesis of an isolable Fe(IV) complex, $Fe(N{=}C^tBu_2)_4$ (**1**), which can be prepared in good yield by oxidation of the Fe(II) ketimide complex, $[Li(THF)]_2[Fe(N{=}C^tBu_2)_4]$, with iodine.[21] Complex **1** is a rare example of a stable Fe(IV) complex and an extremely rare example of an FeX_4-type complex. In fact, MX_4-type complexes of the late first row transition metals (Fe, Co, and Ni) are highly uncommon.[22] To our knowledge, only two other FeX_4-type complexes have appeared in the literature, namely, FeF_4 and $Fe(1\text{-norbornyl})_4$.[23−25] FeF_4 was recently identified by IR spectroscopy in Ar or Ne matrices at cryogenic temperatures.[23] Interestingly, FeF_4 is predicted by density functional theory to exhibit a quintet ground state and a D_{2d} geometry. $Fe(1\text{-norbornyl})_4$ was isolated by Bower and Tennent in 50% yield by reaction of 1-norbornyllithium with $FeCl_3{\cdot}Et_2O$.[24] In the original report, $Fe(1\text{-norbornyl})_4$ was described as a diamagnetic purple crystalline solid; however, it was not fully characterized and the experimental details describing its synthesis were sparse. Nonetheless, it was postulated that $Fe(1\text{-norbornyl})_4$ was formed by disproportionation of a transient Fe(III) or Fe(II) 1-norbornyl complex. Subsequently, Thiele and co-workers reinvestigated the synthesis of $Fe(1\text{-norbornyl})_4$.[26] They prepared $Fe(1\text{-norbornyl})_4$ in modest yield, by reaction of 1-norbornyllithium with $Fe(acac)_3$, and were able to record its ^1H and ^{13}C NMR spectra. Soon after, Theopold and co-workers synthesized the Co analogue, $Co(1\text{-norbornyl})_4$, by reaction of $CoCl_2{\cdot}THF$ with 4 equiv of 1-norbornyllithium.[27−29] They characterized this complex by X-ray crystallography, magnetometry, and cyclic voltammetry and confirmed the low-spin ground state first proposed by Bower and Tennent.[24] Also of note is the synthesis of $Ni(1\text{-norbornyl})_3Br$ by oxidation of $[NBu_4]_2[Ni(1\text{-norbornyl})_3Br]$ with O_2.[30] Finally, we synthesized the homoleptic Co(IV) ketimide, $Co(N{=}C^tBu_2)_4$,[31] further confirming the ability of the ketimide ligand to stabilize the 4+ ions of the late first row transition metals.

Received: May 2, 2013

Scheme 1



Scheme 2



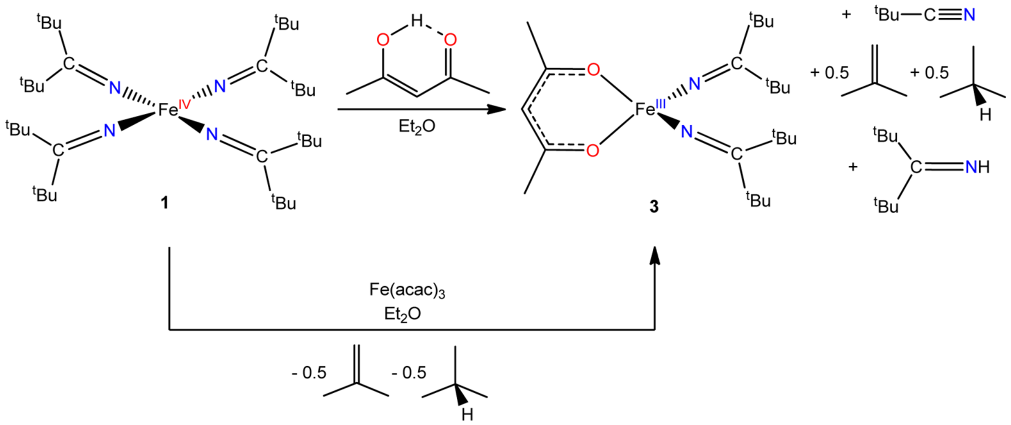
Given the above-mentioned paucity of MX_4-type complexes, we deemed it worthwhile to investigate the reactivity and spectroscopic properties of **1** in further detail. Herein we report a preliminary reactivity study of $Fe(N{=}C^tBu_2)_4$, along with its Mössbauer spectroscopic characterization, in an attempt to evaluate the suitability of $Fe(N{=}C^tBu_2)_4$ as a general purpose synthon for Fe(IV) chemistry. Additionally, we revisited the synthesis of Fe(1-norbornyl)$_4$ and report its solid-state molecular structure and Mössbauer spectrum in an effort to better understand the properties of this elusive oxidation state.

RESULTS AND DISCUSSION

As previously reported,[21] $Fe(N{=}C^tBu_2)_4$ (**1**) can be accessed by oxidation of $[Li(THF)]_2[Fe(N{=}C^tBu_2)_4]$ with elemental iodine in Et_2O. Upon crystallization from a concentrated Et_2O solution, **1** can be easily separated from the LiI byproduct, which is soluble even in cold Et_2O. Using this procedure, complex **1** can be isolated in excellent (93%) yield. This represents an improvement over our original synthesis of **1** which first involved selective precipitation of LiI as its DME adduct followed by crystallization from hexanes.[21] Interestingly, we have also discovered an alternate synthetic route to this molecule that parallels the disproportionation proposed for Fe(1-norbornyl)$_4$. Namely, reaction of $FeCl_3$ with 3 equiv of $Li(N{=}C^tBu_2)$ in THF for 4 h yields a maroon solution from which complex **1** can be isolated in 17% yield (maximum yield of 33% based on iron) (Scheme 1). A second product is also formed in this transformation, $Fe_2(N{=}C^tBu_2)_5$ (**2**), which was identified by comparison of its ^1H NMR spectrum with that of authentic material.[32] This complex was previously isolated by oxidation of $[Li(12\text{-crown-}4)_2][Fe_2(N{=}C^tBu_2)_5]$ with I_2. The formation of **1** and **2** can be rationalized by transient formation of $Fe(N{=}C^tBu_2)_3$, which is unstable under the conditions of the experiment and disproportionates into **1** and $Fe(N{=}C^tBu_2)_2$. $Fe(N{=}C^tBu_2)_2$ is subsequently trapped by $Fe(N{=}C^tBu_2)_3$ to generate complex **2**. The isolation of **1** by disproportionation of the putative $Fe(N{=}C^tBu_2)_3$ intermediate provides further evidence of the strong donating ability of the ketimide ligand. For comparison, the formation of $Cr(N{=}C^tBu_2)_4$ from $CrCl_3$ is also thought to proceed via a similar disproportionation pathway.[33] Likewise, formation of Fe(1-norbornyl)$_4$ from $FeCl_3$ may proceed via disproportionation of an Fe(III) intermediate (see also below).[24]

Unlike many Fe(IV) coordination complexes,[7,16,34] complex **1** is remarkably stable in solution. For example, in C_6D_6, **1** exhibits an approximate half-life of 5 days at room temperature. The decomposition of **1** is first order with respect to $Fe(N{=}C^tBu_2)_4$, with a rate constant of 1.54×10^{-6} s^{-1}. This decomposition can be accelerated by heating a solution of **1** in C_6D_6 at 50 °C for 9 h, yielding a maroon solution. This results in the disappearance of the *tert*-butyl resonance assignable to **1** (at 1.69 ppm) in the ^1H NMR spectrum and the appearance of a new resonance at 10.6 ppm, which we previously assigned to be the mixed valent complex $Fe_2(N{=}C^tBu_2)_5$ (**2**) (Scheme 2).[32] Also observed in this spectrum is the formation of *tert*-butyl cyanide (0.76 ppm), isobutane (1.63 and 0.84 ppm), and

Scheme 3



isobutylene (4.74 and 1.59 ppm) (see the Supporting Information). By integration against an internal standard, the yields of *tert*-butyl cyanide, isobutane, and isobutylene were determined to be 63%, 36%, and 55%, respectively, assuming the stoichiometry suggested in Scheme 2. These products are indicative of the ketimide ligand oxidation and have been observed previously in the decomposition of Mn(N=C^{t}Bu$_2$)$_4$.[35] To account for the formation of the observed products, we suggest that homolysis of the C−C bond in the ketimide ligand of **1** results in formation of "Fe(N=C^{t}Bu$_2$)$_3$", *tert*-butylcyanide and the *tert*-butyl radical. Subsequent disproportionation of the *tert*-butyl radical results in formation of isobutylene and isobutane,[35−38] while Fe(N=C^{t}Bu$_2$)$_3$ undergoes the disproportionation described in Scheme 1. On a preparative scale, thermolysis of **1** in Et$_2$O at 50 °C for 8 h provides **2** in 40% yield.[32] Interestingly, complex **2** can also be formed by heating a mixture of FeCl$_3$ and 3 equiv of Li(N=C^{t}Bu$_2$) in Et$_2$O at 55 °C for 18 h. Under these conditions, **2** can be isolated in a 72% yield.

To further support the proposed decomposition mechanism of **1**, we endeavored to trap the transient *tert*-butyl radical intermediate with P$_4$. It has been previously shown that P$_4$ is an effective trap for organic radicals.[39,40] Thus, thermolysis of **1** at 50 °C in the presence of 0.25 equiv of P$_4$ for 29 h in C$_6$D$_6$ yields P^{t}Bu$_3$ as the sole phosphorus-containing product (Scheme 2) in addition to the anticipated formation of **2** and *tert*-butyl cyanide. The generation of P^{t}Bu$_3$ was confirmed by observation of a singlet in the ^{31}P NMR spectrum at 64.2 ppm, consistent with previously reported literature values.[41] Similarly, a doublet at 31.3 ppm (J_{PC} = 6.2 Hz) in the ^{13}C NMR spectrum is also assignable to P^{t}Bu$_3$.[41] Importantly, there is no formation of isobutane or isobutylene in this sample according to ^{1}H NMR spectroscopy. This supports our hypothesis that P$_4$ captures the *tert*-butyl radical before it can undergo disproportionation.

To evaluate the suitability of complex **1** as a synthon for Fe(IV) chemistry, we undertook a series of simple ligand exchange reactions, given that the strongly basic ketimide anion should be readily amenable to protonation. Thus, reaction of **1** with 1 equiv of acetylacetone (Hacac) generates a purple solution from which the Fe(III) ketimide complex, Fe(N=C^{t}Bu$_2$)$_2$(acac) (**3**), can be isolated as a purple crystalline solid in 50% yield (Scheme 3). The ^{1}H NMR spectrum of **3** in C$_6$D$_6$ consists of a very broad resonance at 59.2 ppm, assignable to the *tert*-butyl groups of the ketimide ligand, while a broad resonance at −8.2 ppm is assignable to the methyl groups of the acac ligand. Also observed in this reaction mixture are bis(*tert*-butyl)ketimine, isobutane, isobutylene, and *tert*-butyl cyanide. To account for the formation of isobutane and isobutylene, we suggest that ketimide protonation initially generates the putative intermediate "Fe(N=C^{t}Bu$_2$)$_3$(acac)", whose ligand set, with only three ketimide ligands, is unable to support the 4+ oxidation state. Subsequent ligand oxidation generates complex **3**, *tert*-butyl cyanide, and the *tert*-butyl radical. Alternately, the change in geometry required to form this 5-coordinate species could induce oxidation of a ketimide ligand. Monitoring the formation of **3** by ^{1}H NMR spectroscopy reveals the presence of complex **1** and Fe(acac)$_3$ at short reaction times. The presence of Fe(acac)$_3$ was confirmed by comparison of its ^{1}H NMR spectrum with that of authentic material. At longer reaction times (21 h) this mixture completely converts to complex **3**, suggesting that complex **1** and Fe(acac)$_3$ undergo ligand exchange to generate the final product. In support of this hypothesis, complex **3** can also be formed by the reaction of 0.5 equiv of Fe(acac)$_3$ with **1** at 25 °C in Et$_2$O (Scheme 3).

Crystals of **3** suitable for X-ray crystallographic analysis were grown from a concentrated Et$_2$O solution at −25 °C. Complex **3** crystallizes in the triclinic space group $P\bar{1}$ and exhibits a distorted tetrahedral environment about the Fe center [e.g., N1−Fe1−N2 = 113.28(7)°, N2−Fe1−O1 = 109.36(6)°, O1−Fe1−O2 = 90.98(5)°] (Figure 1). The Fe−N bond lengths are 1.8404(16) and 1.8456(16) Å, which are slightly shorter than those observed previously for Fe(III) ketimides, but are nonetheless consistent with the Fe^{3+} oxidation-state assignment.[21] In addition, the Fe−N−C angles in **3** [159.53(15)° and 176.31(15)°] are suggestive of π-donation to the metal center. Finally, the Fe−O bond lengths [Fe1−O1 = 1.9736(12) Å and Fe1−O2 = 1.9740(13) Å] are in line with those observed previously for Fe^{3+} acetylacetonate complexes.[42,43]

Given the paucity of stable FeX$_4$-type complexes, we revisited the synthesis of Fe(1-norbornyl)$_4$ in an effort to complete its characterization. Thus, addition of 3 equiv of 1-norbornyllithium to a solution of FeCl$_3$ in 1:10 Et$_2$O/pentane at −25 °C generates a deep purple solution and a black precipitate after 4 h of stirring (Scheme 4). Filtration of this mixture through an alumina column followed by extraction of the material in MeCN and crystallization from MeCN/Et$_2$O yields Fe(1-norbornyl)$_4$ (**4**) as a deep purple solid in 25% yield (based upon 1-norbornyllithium). We have found that filtration through alumina is effective for removing excess 1-norbornyllithium from the reaction mixture, while recrystallization of **4**

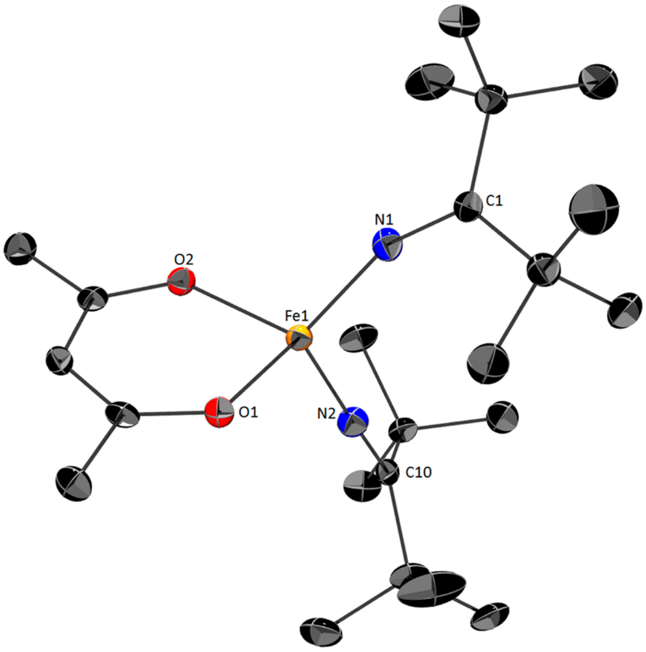


Figure 1. Solid-state molecular structure of Fe(N$=$C^{t}Bu$_2$)$_2$(acac) (**3**) with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Fe1−N1 = 1.8456(16), Fe1−N2 = 1.8404(16), Fe1−O1 = 1.9736(12), Fe1−O2 = 1.9740(13); N1−Fe1−N2 = 113.28(7), N2−Fe1−O1 = 109.36(6), O1−Fe1−O2 = 90.98(5).

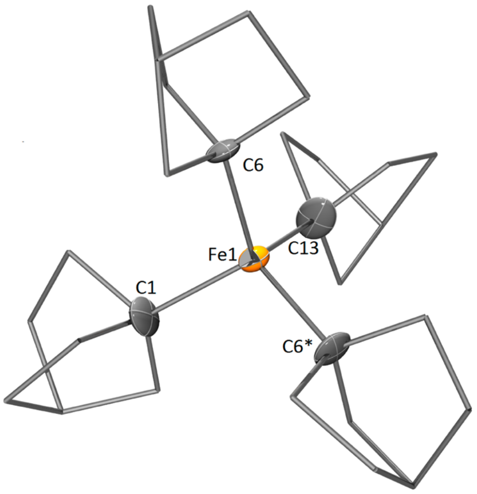
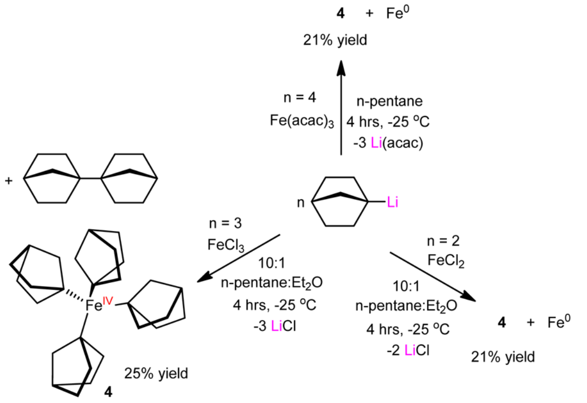


Figure 2. Solid-state molecular structure of Fe(1-norbornyl)$_4$ (**4**) with 50% thermal ellipsoids for selected atoms. Selected bond lengths (Å) and angles (deg): Fe1−C1 = 2.002(14), Fe1−C6 = 1.984(7), Fe1−C13 = 2.002(9); C1−Fe1−C6 = 109.4(3), C6−Fe1−C13 = 109.7(3).

Scheme 4



from MeCN/Et$_2$O provides material that is free of 1,1′-binorbornyl (see below).

The ^{1}H NMR spectrum of **4** in C$_6$D$_6$ exhibits a characteristic resonance at 2.33 ppm, assignable to the bridgehead CH group at position 4 of the norbornyl skeleton, while its ^{13}C NMR spectrum agrees with that obtained by Thiele and co-workers.[26] Single crystals of **4** suitable for X-ray diffraction analysis were obtained from a concentrated pentane solution at −25 °C. Fe(1-norbornyl)$_4$ crystallizes in the orthorhombic space group *Pmn*2$_1$ (Figure 2) and is isomorphous with its Co analogue.[29] As was observed for Co(1-norbornyl)$_4$, the 1-norbornyl ligands in **4** are disordered over multiple positions, a consequence of facile rotation about the Fe−C bond. The Fe center exhibits a nearly idealized tetrahedral coordination environment about the iron center [C1−Fe1−C6 = 109.4(3)°, C6−Fe1−C13 = 109.7(3)°]. The M−C bond lengths range between 1.984(7) and 2.002(14) Å and are longer than the Co−C bond lengths in Co(1-norbornyl)$_4$, which range between 1.912(23) and 1.930(21) Å, consistent with the larger ionic radius of Fe^{4+}. The Fe−C bond lengths of **4** are also longer than those observed for Ni(1-norbornyl)$_3$Br (av. 1.93 Å).[30] The nearly perfect tetrahedral geometry of complex **4**, coupled with the apparent diamagnetism, demonstrates that 1-norbornyl is an unusually strong field ligand, given that all four d electrons are forced into the d_{z^2} and $d_{x^2-y^2}$ orbitals. The strong field nature of 1-norbornyl was previously noted by Theopold and co-workers, who determined Δ_t for a series of cobalt 1-norbornyl complexes.[27]

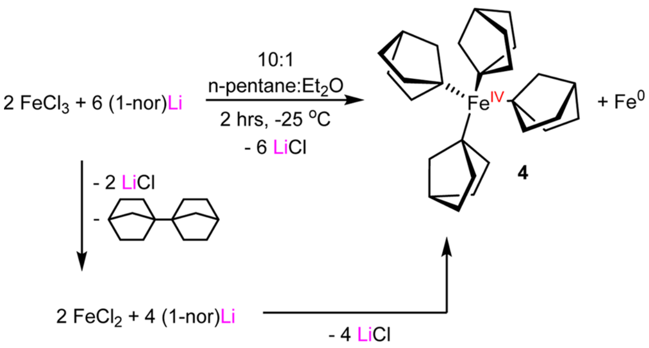
An aliquot of the crude reaction mixture, in C$_6$D$_6$, reveals the presence of three identifiable species, namely, complex **4**, 1-norbornyllithium, and 1,1′-binorbornyl in an approximately 1:3:1 ratio, respectively, according to ^{1}H NMR spectroscopy. These materials were readily identified by their characteristic bridgehead proton resonances, which appear at 2.33, 2.51, and 2.17 ppm for **4**, 1-norbornyllithium, and 1,1′-binorbornyl, respectively.[30] The formation of 1,1′-binorbornyl can be rationalized by the coupling of two 1-norbornyl radicals, formed by oxidation of 1-norbornyllithium by FeCl$_3$.[44] The presence of 1-norbornyllithium, the dominant 1-norbornyl-containing species in solution, is more challenging to explain given the 3:1 stoichiometry of the reaction and suggests that unreacted iron halides are sequestered within the black precipitate.

Complex **4** could also be prepared by reaction of FeCl$_2$ with 2 equiv of 1-norbornyllithium in a 1:10 mixture of Et$_2$O/pentane (Scheme 4). Under these conditions, **4** can be isolated in 21% yield. Also formed in the reaction are Fe metal, present as a fine black powder that adheres to the stir bar, and 1,1′-binorbornyl, which was observed in the crude reaction mixture by ^{1}H NMR spectroscopy (Supporting Information, Figure S24). We also repeated the synthetic procedure reported by Thiele,[26] namely, reaction of Fe(acac)$_3$ with 4 equiv of 1-norbornyllithium in pentane, and were able to isolate **4** in 21% yield (Scheme 4). We also observed formation of small amounts of 1,1-binorbornyl in the reaction mixture, according to ^{1}H NMR spectroscopy (Supporting Information, Figure S26). The choice of solvent in both reactions appears to be crucial for success. For example, the presence of Et$_2$O in the

$FeCl_2$ reaction is critical for the formation of **4** because in pure pentane, the reaction is extremely slow and the yields of **4** are greatly reduced. However, in the case of $Fe(acac)_3$, the reaction must be performed in pure pentane, as the presence of any Et_2O results in formation of an intractable mixture of products.

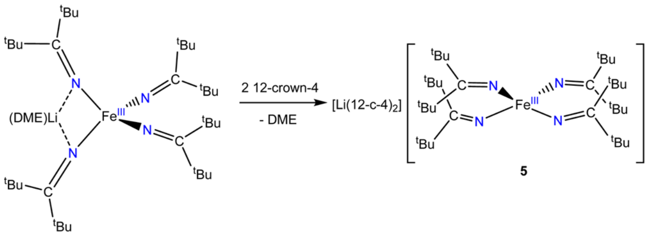
Given the above evidence, we suggest that complex **4** is formed by disproportionation of a transient Fe(III) 1-norbornyl complex, resulting in concomitant formation of Fe(0) or other low-valent Fe-containing products. A similar conclusion was reached by both Bower and Theopold in their investigations of 1-norbornyllithium with metal salts.[24,27] Alternately, reduction of Fe^{3+} to Fe^{2+} by 1-norbornyllithium may be a necessary first step along the reaction pathway. This is followed by disproportionation of the Fe^{2+} ion to Fe(IV) and Fe(0) (Scheme 5). This hypothesis is supported by the observation that $FeCl_2$ is also a viable starting material for the formation of **4** and by the presence of 1,1′-binorbornyl in the $FeCl_3$ reaction mixture.

Scheme 5



For further spectroscopic comparison, we also synthesized a nearly isostructural Fe(III) analogue of complex **1**. Thus, reaction of $[Li(DME)][Fe(N{=}C^tBu_2)_4]$[21] with 2 equiv of 12-crown-4 yields $[Li(12\text{-crown-}4)_2][Fe(N{=}C^tBu_2)_4]$ (**5**) as a maroon solid in 84% yield (Scheme 6). The ^1H NMR spectrum of **5** in py-d_5 at −36 °C features a broad singlet at 31.1 ppm, assignable to the methyl groups of the ketimide ligand, while its −36 °C ^7Li NMR spectrum consists of a broad singlet at 3.4 ppm, assignable to the $[Li(12\text{-crown-}4)_2]$ cation. When the sample is heated to room temperature, the resonance at 31.1 ppm in the ^1H NMR spectrum decreases in intensity, while new resonances appear at 46.9 and 37.8 ppm. Similar behavior was observed previously for the Co analogue, $[Li(12\text{-crown-}4)_2][Co(N{=}C^tBu_2)_4]$,[31] and was rationalized by invoking an equilibrium between $[Li(12\text{-crown-}4)_2][Co(N{=}C^tBu_2)_4]$ and a close contact ion pair formed by loss of 12-crown-4 and coordination of Li^+ by the nitrogen atoms of the ketimide ligands.[31]

Scheme 6



In the solid state, complex **5** exhibits a squashed tetrahedral geometry (e.g., N1−Fe1−N2 = 145.02(14)°, τ_4 = 0.50)[45] (Figure 3). Its Fe−N bond lengths are 1.858(4) and 1.859(3) Å, while the ketimide ligands are bound in a distinctly nonlinear fashion (Fe1−N1−C1 = 154.9(3)°, Fe1−N2−C10 = 156.6(3)°). The Fe−N bond lengths in **5** are ca. 0.05 Å shorter than those observed in the isostructural Mn(III) analogue, $[Li(12\text{-crown-}4)_2][Mn(N{=}C^tBu_2)_4]$,[35] likely a consequence of the smaller ionic radius of Fe^{3+}. However, the metrical parameters of **5** are nearly identical to those exhibited by the Co(III) analogue, $[Li(12\text{-crown-}4)_2][Co(N{=}C^tBu_2)_4]$.[31] Finally, solid-state superconducting quantum interference device (SQUID) magnetometry measurements reveal that complex **5** exhibits an effective magnetic moment of 3.85 μ_B at 300 K, consistent with an $S = 3/2$ ground state. This spin state contrasts with the high-spin $S = 5/2$ ground state of $[Li(DME)][Fe(N{=}C^tBu_2)_4]$, which possesses a slightly distorted tetrahedral geometry.[21] However, the intermediate $S = 3/2$ spin state of complex **5** is identical to that observed for the isoelectronic Co(IV) complex, $Co(N{=}C^tBu_2)_4$,[31] suggesting that complex **5** features a similar d orbital splitting pattern.

Mössbauer Spectroscopy. To confirm the 4+ oxidation-state assignments in complexes **1** and **4**, we recorded their zero-field ^{57}Fe Mössbauer spectra at 80 K. For further comparison, we also recorded the zero-field ^{57}Fe Mössbauer spectra of complex **5** and the previously reported Fe(II) ketimide, $[Li(THF)]_2[Fe(N{=}C^tBu_2)_4]$ (**6**).[21] The zero-field ^{57}Fe Mössbauer spectra of **1** and **4** are shown in Figure 4, while relevant spectral parameters are summarized in Table 1. Complex **1** features a single quadrupole doublet with parameters of δ = −0.15 mm/s and ΔE_Q = 1.62 mm/s. The low value for the isomer shift is consistent with the 4+ oxidation-state assignment and compares well with isomer shifts recorded for a variety of authentic Fe(IV) complexes (Table 1).[14,34,46−48] The Mössbauer spectrum of the Fe(III) analogue, **5**, consists of two quadrupole doublets in a 93:7 ratio. The major component is assignable to **5** and features parameters of δ = 0.19 mm/s and ΔE_Q = 3.56 mm/s (see the Supporting Information). The minor component is assignable to **1**, which is likely formed by oxidation of **5** by adventitious O_2 during sample handling. The isomer shift of **5** is consistent with reported $S = 3/2$ Fe(III) compounds, although other iron oxidation and spin states may also be found in this range.[49] The asymmetry of the spectrum is also consistent with half-integer spin.[49−51] The Mössbauer spectrum of **6** also consists of two quadrupole doublets, in a 85:15 ratio. The major component, which is assignable to **6**, features parameters of δ = 0.44 mm/s and ΔE_Q = 0.85 mm/s. Again, the minor component is assignable to complex **1**. Most importantly, a comparison of the isomer shifts of **6**, **5**, and **1** reveals a periodic decrease in isomer shift as the Fe oxidation state is increased, in full accord with our proposed oxidation-state assignments.

The Mössbauer spectrum of complex **4** exhibits an absorption modeled with spectral parameters of δ = −0.28 mm/s and ΔE_Q = 0.15 mm/s. The low isomer shift of **4** is consistent with the 4+ oxidation-state assignment,[14,34,46−48] while the near zero ΔE_Q is suggestive of a spherical electric field gradient tensor.[52] This latter parameter is in line with the tetrahedral geometry of **4**, as determined by X-ray crystallography, and unambiguously identifies complex **4** as a low-spin Fe(IV) complex.

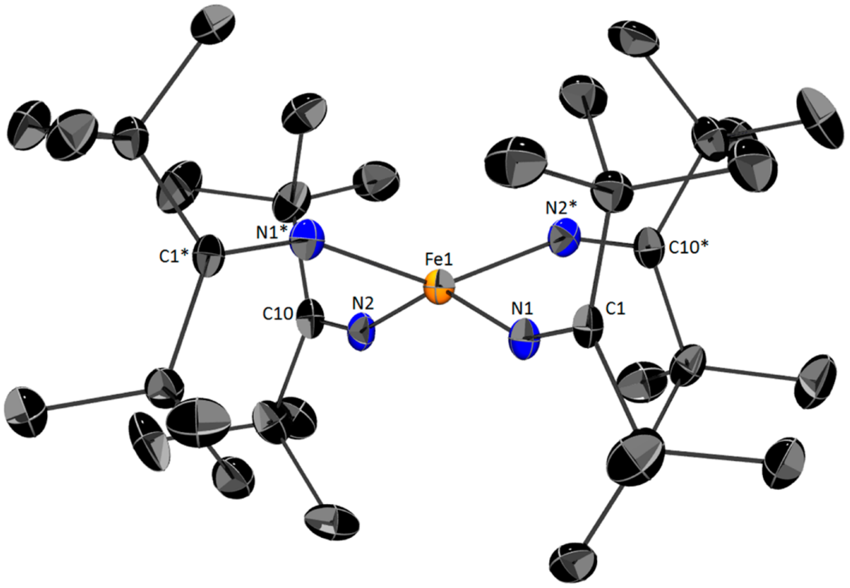


Figure 3. Solid-state molecular structure of $[Li(12\text{-crown-}4)_2][Fe(N{=}C^tBu_2)_4]$ (**5**) with 40% probability ellipsoids. $[Li(12\text{-crown-}4)_2]^+$ and hydrogen atoms are excluded for clarity. Atoms with an asterisk are generated by symmetry. Selected bond lengths (Å) and angles (deg): Fe1−N1 = 1.859(3), Fe1−N2 = 1.858(4); N1−Fe1−N2 = 145.02(14), N1−Fe1−N1* = 94.0(2), Fe1−N1−C1 = 154.9(3), Fe1−N2−C10 = 156.6(3).

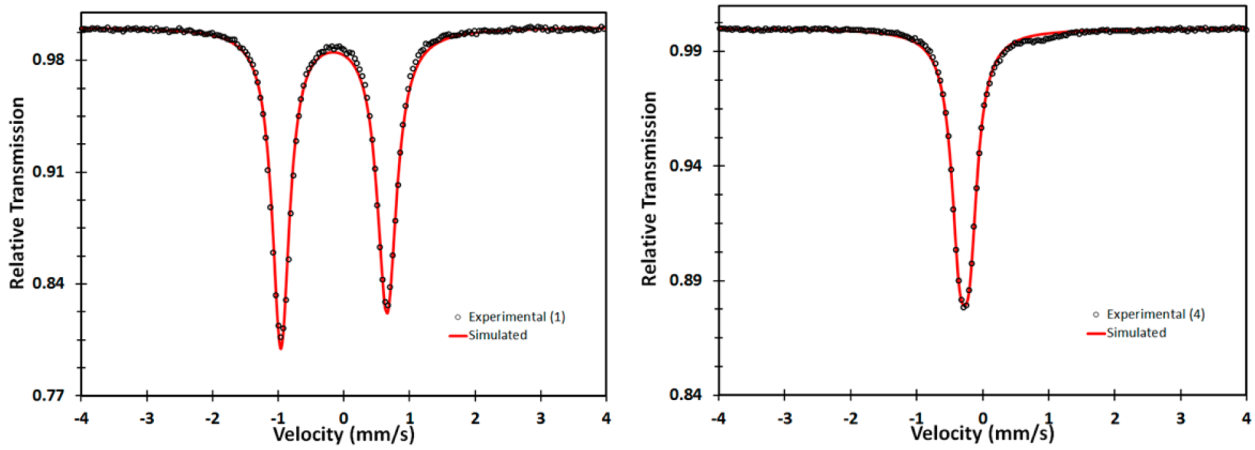


Figure 4. Solid-state zero-field ^{57}Fe Mössbauer spectra of complexes **1** (left) and **4** (right) collected at 80 K.

Table 1. Mössbauer Data for Complexes 1 and 4−6 and Selected Fe(IV) Complexes

complex[a]	δ (mm/s)	ΔE_Q (mm/s)	oxidation state	S	ref
$[Li(THF)]_2[Fe(N{=}C^tBu_2)_4]$ (**6**)	0.44	0.85	2	2	*b*
$[Li(12\text{-crown-}4)_2][Fe(N{=}C^tBu_2)_4]$ (**5**)	0.19	3.56	3	3/2	*b*
$Fe(N{=}C^tBu_2)_4$ (**1**)	−0.15	1.62	4	0	*b*
Fe(1-norbornyl)$_4$ (**4**)	−0.28	0.15	4	0	*b*
$[Fe(F)(Me_3\text{cyclam-acetate})]^{2+}$	0.02	2.43	4	1	52,53
$[Fe(N_3)(Me_3\text{cyclam-acetate})]^{2+}$	0.11	1.92	4	1	53
$Fe(N)(PhB(^tBuIm)_3)$	−0.28	6.23	4	0	48
$[Fe(TAML)Cl]^-$	−0.04	0.89	4	2	54
$[Fe(TAML)(CN^tBu)_2]$	−0.04	3.38	4	1	54
$[Fe(N)(PhBP^{iPr}_3)]$	−0.34	6.01	4	0	34,55

[a] Ligand definitions: Me_3cyclam-acetate = 4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane-1-acetate; TAML = 1,4,8,11-tetraaza-13,13-diethyl-2,2,5,5,7,7,10,10-octamethyl-3,6,9,12,14-pentaoxocyclotetradecane; $[PhB(^tBuIm)_3]^-$ = phenyltris(3-*tert*-butylimidazol-2-ylidene)borato; $PhBP^{iPr}_3$ = $[PhB(CH_2P^iPr_2)_3]^-$. [b] This work.

■ CONCLUSION

We have provided further detail regarding the synthesis and characterization of the homoleptic Fe(IV) ketimide, $Fe(N{=}C^tBu_2)_4$. Importantly, its Mössbauer spectrum confirms the 4+ oxidation-state assignment. Upon being heated gently, $Fe(N{=}C^tBu_2)_4$ converts into the mixed valent Fe(III/II) complex, $Fe_2(N{=}C^tBu_2)_5$. Also formed in the reaction are the products of ketimide ligand oxidation, *tert*-butylcyanide, isobutane, and isobutylene. Similarly, reaction of $Fe(N{=}C^tBu_2)_4$ with acetylacetone results in formation of a lower-valent Fe complex, namely, $Fe(N{=}C^tBu_2)_2(acac)$, along with the products of ketimide oxidation. Because reduction of the Fe^{4+} center in $Fe(N{=}C^tBu_2)_4$ is apparently quite facile, it appears unlikely that this complex will be a useful synthon for Fe(IV) chemistry. It is clear that the development of a ketimide-based Fe(IV) synthon will require a reassessment of the ligand architecture as the bis(*tert*-butyl)ketimide ligand is too easily oxidized. There is no doubt that the relative stability of the *tert*-butyl radical plays a role in lowering the activation barrier of the decomposition process,[56] and for future work we plan to improve the stability of the ketimide ligand by employing alkyl substituents that are not as likely to undergo unwanted C−C bond homolysis. Finally, we revisited the synthesis of Fe(1-norbornyl)$_4$ and confirmed its formulation with X-ray crystallography and Mössbauer spectroscopy. Its low isomer shift and near zero quadrupolar splitting verify the low-spin d^4 ground state and provide further data for relating Mössbauer spectroscopic parameters to the electronic structure of high-valent Fe systems.

■ EXPERIMENTAL SECTION

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen or argon. THF, hexanes, diethyl ether, and toluene were dried using a Vacuum Atmospheres DRI-SOLV solvent purification system. C_6D_6 and DME were dried over activated 3 Å molecular sieves for 24 h before use. $Li(N{=}C^tBu_2)$ and 1-norbornyllithium were synthesized according to the previously reported procedures,[27,57,58] while all other reagents were purchased from commercial suppliers and used as received.

^1H, $^{13}C\{^1H\}$, and $^7Li\{^1H\}$ NMR spectra were recorded on a Varian UNITY INOVA 400, Varian UNITY INOVA 500, or Varian UNITY INOVA 600 spectrometer. ^1H NMR spectra are referenced to the residual protio solvent peaks as internal standards. $^7Li\{^1H\}$ spectra were referenced to external LiCl in D_2O. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. UV−vis/NIR experiments were performed on a UV-3600 Shimadzu spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory at University of California (Berkeley, CA).

Magnetism Measurements. Magnetism data were recorded using a Quantum Design MPMS 5XL SQUID magnetometer. Complex **5** was analyzed using 50 mg of powdered crystalline material loaded into a NMR tube, which was subsequently flame-sealed. The solid was kept in place with ∼45 mg of quartz wool packed on either side of the sample. Data for complex **5** were collected using a 1 T field between 4 and 300 K. Diamagnetic correction for **5**, $\chi_{dia} = -7.09 \times 10^{-4}$ cm^3 mol^{-1}, was made using Pascal's constants.[59]

Mössbauer Measurements. Zero-field ^{57}Fe Mössbauer spectra were collected at Princeton University on a SEE Co. Mössbauer spectrometer (MS4) with a $^{57}Co/Rh$ radiation source at 80 K in constant acceleration mode. The temperature in the sample chamber was controlled by a Janis Research Co. CCS-850 He/N_2 cryostat within an accuracy of ±0.3 K. The data were calibrated relative to an α-iron standard at 298 K, with minimum experimental line widths of 0.23 mm/s. The fitting procedure to extract quantitative spectral parameters uses a least-squares Lorentzian fitting method using the WMOSS software developed by SEE Co.

Synthesis of $Fe(N{=}C^tBu_2)_4$ (1). To a stirring solution of $[Li(THF)]_2[Fe(N{=}C^tBu_2)_4]$ (1.402 g, 1.81 mmol) in Et_2O (10 mL) was added dropwise I_2 (0.465 g, 1.82 mmol) as an Et_2O solution (5 mL). After 30 min of being stirred, the deep orange solution was concentrated in vacuo to 10 mL. Subsequent storage at −25 °C for 24 h resulted in the deposition of dark crystals, which were isolated by decanting off the supernatant (1.029 g, 93% yield). This material was spectroscopically identical to an authentic sample of $Fe(N{=}C^tBu_2)_4$.[21]

Monitoring of the Thermal Stability of $Fe(N{=}C^tBu_2)_4$ (1) by NMR Spectroscopy. $Fe(N{=}C^tBu_2)_4$ (8.0 mg, 0.013 mmol) and hexamethyldisiloxane (3 μL, 14 μmol) were dissolved in C_6D_6 (0.7 mL), yielding a red-brown solution. The decomposition of **1** and formation of **2**, ^tBuCN, isobutane, and isobutylene at 25 °C were monitored over 16 days. The yields of ^tBuCN, isobutane, and isobutylene were determined by integration against the hexamethyldisiloxane internal standard.

Thermolysis of $Fe(N{=}C^tBu_2)_4$ (1). $Fe(N{=}C^tBu_2)_4$ (9.3 mg, 0.015 mmol) was dissolved in C_6D_6 (0.5 mL), yielding a red-brown solution. The J-Young NMR tube was heated for 9 h at 50 °C, yielding a maroon solution containing **2**, isobutane, isobutylene, and ^tBuCN. ^1H NMR (C_6D_6, 25 °C, 400 MHz) δ: 10.6 (br s, $Fe_2(N{=}C^tBu_2)_5$), 4.74 (s, $(CH_3)_2CCH_2$), 1.63 (m, $(CH_3)_3CH$), 1.59 (s, $(CH_3)_2CCH_2$), 0.84 (d, J_{HH} = 5.6 Hz, $(CH_3)_3CH$), 0.76 (s, $(CH_3)_3CCN$).

Thermolysis of $Fe(N{=}C^tBu_2)_4$ in the Presence of P_4. $Fe(N{=}C^tBu_2)_4$ (9.0 mg, 0.015 mmol) was dissolved in C_6D_6 (0.5 mL), yielding a red-brown solution. To this solution was added a solution of P_4 in C_6D_6 (35 μL, 0.1126 M, 0.004 mmol of P_4). The J-Young NMR tube was heated for 29 h at 50 °C, yielding a maroon solution containing **2**,[32] P^tBu_3, and ^tBuCN. Formation of P^tBu_3 was confirmed by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies. ^1H NMR (C_6D_6, 25 °C, 400 MHz) δ: 0.76 (s, ^tBuCN), 1.35 (s, P^tBu_3), 10.57 (br s, $Fe_2(N{=}C^tBu_2)_5$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 100 MHz) δ: 64.22 (s, P^tBu_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 100 MHz) δ: 27.67 (s, ^tBuCN), 31.29 (d, J_{PC} = 6.2 Hz, $P(C(CH_3)_3)_3$). The quaternary carbon resonances of P^tBu_3 and ^tBuCN were not observed.

Synthesis of $Fe_2(N{=}C^tBu_2)_5$ (2) via $FeCl_3$. $FeCl_3$ (172 mg, 1.0 mmol) was added to a stirring solution of $Li(N{=}C^tBu_2)$ (415 mg, 3.23 mmol) in Et_2O (15 mL). After 24 h of being stirred, the maroon solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm). The filtrate was dried in vacuo, and a ^1H NMR spectrum in C_6D_6 was recorded. ^1H NMR (C_6D_6, 25 °C, 400 MHz) δ: 10.51 (br s, $Fe_2(N{=}C^tBu_2)_5$), 1.69 (s, $Fe(N{=}C^tBu_2)_4$). The resulting solid was dissolved in hexanes (10 mL) and heated for 18 h at 55 °C to yield a maroon solution. The maroon solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm). The filtrate was concentrated in vacuo to 1 mL. Subsequent storage at −25 °C for 24 h resulted in the deposition of maroon blocks, which were isolated by decanting off the supernatant (273 mg, 72% yield). ^1H NMR (C_6D_6, 25 °C, 400 MHz) δ: 10.59 (br s, $Fe_2(N{=}C^tBu_2)_5$). This material was spectroscopically identical to an authentic sample of $Fe_2(N{=}C^tBu_2)_5$.[32]

Synthesis of $Fe_2(N{=}C^tBu_2)_5$ (2) by Thermolysis of $Fe(N{=}C^tBu_2)_4$ (1). $Fe(N{=}C^tBu_2)_4$ (39.5 mg, 0.064 mmol) was dissolved in C_6D_6 (0.5 mL), yielding a red-brown solution. The J-Young NMR tube was heated for 8 h at 50 °C, yielding a maroon solution. ^1H NMR (C_6D_6, 25 °C, 400 MHz) δ: 10.7 (br s, $Fe_2(N{=}C^tBu_2)_5$), 4.74 (s, $(CH_3)_2CCH_2$), 1.63 (m, $(CH_3)_3CH$), 1.58 (s, $(CH_3)_2CCH_2$), 0.84 (d, $(CH_3)_3CH$), 0.77 (s, $(CH_3)_3CCN$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 100 MHz) δ: 141.90 (s, $(CH_3)_2CCH_2$), 111.11 (s, $(CH_3)_2CCH_2$), 30.15 (s, $(CH_3)_3CCN$), 27.10 (s, $(CH_3)_3CCN$), 25.86 (s, $(CH_3)_3CH$), 24.86 (s, $(CH_3)_3CH$), 24.14 (s, $(CH_3)_2CCH_2$). The solvent was removed in vacuo, and the solid was dissolved into hexanes (1 mL). The maroon solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm). Storage of this solution at −25 °C for 5 h resulted in the deposition of dark blocks, which were isolated by decanting off the supernatant (10.2 mg, 40% yield). This material was spectroscopically identical to an authentic sample of $Fe_2(N{=}C^tBu_2)_5$.[32]

Synthesis of $Fe(N{=}C^tBu_2)_4$ (1) via $FeCl_3$. $FeCl_3$ (24.5 mg, 0.15 mmol) was added to a stirring solution of $Li(N{=}C^tBu_2)$ (67.0 mg, 0.46 mmol) in THF (2 mL). After 4 h of being stirred, the maroon solution was dried in vacuo, and the resulting solid was dissolved in hexanes (2 mL). The maroon solution was then filtered through a Celite column supported on glass wool (0.5 × 2 cm). The filtrate was concentrated in vacuo to 1 mL. Subsequent storage at −25 °C for 24 h resulted in the deposition of dark blocks, which were isolated by decanting off the supernatant (12.2 mg, 17% yield, maximum yield of 33% based on iron). This material was spectroscopically identical to an authentic sample of $Fe(N{=}C^tBu_2)_4$.[21]

Synthesis of $Fe(N=C^tBu_2)_2(acac)$ (3). *Method A.* To a stirring red-orange solution of $Fe(N=C^tBu_2)_4$ (**1**) (103 mg, 0.17 mmol) in Et_2O (2 mL) was added an orange solution of $Fe(acac)_3$ (28.3 mg, 0.084 mmol) in Et_2O (2 mL). After 21 h of being stirred, the deep purple solution was filtered through a Celite column supported on glass wool (0.5 × 2 cm). The filtrate was concentrated in vacuo to 1 mL. Subsequent storage at −25 °C for 24 h resulted in the deposition of purple blocks, which were isolated by decanting off the supernatant (58 mg, 53% yield). Anal. Calcd for $FeN_2O_2C_{23}H_{43}$: C, 63.44; H, 9.95; N, 6.43. Found: C, 63.14; H, 9.97; N, 6.26.

Method B. To a red-orange solution of $Fe(N=C^tBu_2)_4$ (**1**) (39.9 mg, 0.065 mmol) in toluene (3 mL) was added acetylacetone (7 μL, 0.09 mmol). After 16 h of being stirred, a deep purple solution was obtained, and the solvent was removed in vacuo. The purple solid was extracted into hexanes (1 mL). Subsequent storage at −25 °C for 24 h resulted in the deposition of purple blocks, which were isolated by decanting off the supernatant (14.2 mg, 50% yield). ^1H NMR (C_6D_6, 25 °C, 400 MHz) δ: 59.2 (br s, 36H, $Fe(N=C^t\mathit{Bu}_2)(acac)$), −8.2 (br s, 6H, $Fe(N=C^tBu_2)(O(\mathit{CH}_3)CH(\mathit{CH}_3)O)$). IR ($Et_2O$, cm^{-1}): 1654 (s, ν(N=C)), 1579 (m, ν(N=C)).

Monitoring the Formation of $Fe(N=C^tBu_2)_2(acac)$ (3) by NMR Spectroscopy. To a red-orange solution of $Fe(N=C^tBu_2)_4$ (**1**) (8 mg, 0.02 mmol) in C_6D_6 (0.5 mL) was added acetylacetone (2.5 μL, 0.03 mmol). After 10 min, a deep orange solution was obtained, and a ^1H NMR spectrum was recorded. ^1H NMR (C_6D_6, 25 °C, 400 MHz) δ: 20.3 (br s, 18H, $Fe(O(\mathit{CH}_3)CH(\mathit{CH}_3)O)_3$), −23.8 (br s, 3H, $Fe(O(CH_3)\mathit{CH}(CH_3)O)_3$). The formation of $Fe(acac)_3$ was confirmed by comparison to the ^1H NMR spectrum of commercially prepared $Fe(acac)_3$. The reaction mixture was allowed to stand, and after 21 h the ^1H NMR spectrum of the now deep purple solution was recorded. ^1H NMR (C_6D_6, 25 °C, 400 MHz) δ: 59.2 (br s, 36H, $Fe(N=C^t\mathit{Bu}_2)(acac)$), −8.2 (br s, 6H, $Fe(N=C^tBu_2)(O(\mathit{CH}_3)CH(\mathit{CH}_3)O)$). The γ-proton on the acetylacetonate ligand was not observed in the ^1H NMR spectra.

Synthesis of $Fe(1\text{-norbornyl})_4$ from $FeCl_3$. To a cold (−25 °C), stirring, yellow solution of $FeCl_3$ (45.7 mg, 0.28 mmol) in a mixture of Et_2O (0.2 mL) and pentane (2 mL) was added a cold (−25 °C) solution of 1-norbornyllithium (83.9 mg, 0.82 mmol) in pentane (4 mL). The solution immediately turned deep purple, concomitant with the deposition of a fine black precipitate. The reaction mixture was allowed to stir for 4 h, whereupon the mixture was filtered through a basic alumina column supported on glass wool (0.5 × 3 cm). The volume of the deep purple filtrate was reduced in vacuo to 1 mL and layered on acetonitrile (12 mL). Storage at −25 °C for 24 h resulted in the deposition of a dark purple solid. The solid was isolated by decanting off the supernatant (22.7 mg, 25% yield based upon 1-norbornyllithium). Anal. Calcd for $FeC_{28}H_{44}$: C, 77.05; H, 10.16. Found: C, 76.73; H, 9.98. ^1H NMR (benzene-d_6, 25 °C, 600 MHz) δ: 0.98−1.2 (m, 24H), 1.45 (br s, 8H), 1.58 (br s, 8H), 2.33 (br s, 4H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 25 °C, 150 MHz) δ: 30.25 (C3, C5), 33.07 (C2, C6), 34.66 (C4), 42.73 (C7), 51.39 (C1). IR (KBr mull, cm^{-1}): 742 (m), 829 (w), 921 (w), 972 (m), 1087 (m), 1138 (m), 1206 (m), 1245 (m), 1280 (m), 1300 (m), 1314 (m).

Synthesis of $Fe(1\text{-norbornyl})_4$ from $FeCl_2$. To a cold (−25 °C) stirring suspension of $FeCl_2$ (39.2 mg, 0.31 mmol) in a mixture of Et_2O (1 mL) and pentane (4 mL) was added a cold (−25 °C) solution of 1-norbornyllithium (63.3 mg, 0.62 mmol) in pentane (6 mL). The solution was allowed to stir for 45 min, whereupon the color became deep purple and a fine black solid was deposited. This solid adhered to the stir bar once the stirring was stopped. The mixture was filtered through a basic alumina column supported on glass wool (0.5 × 3 cm). The solvent was removed in vacuo, and the purple solid was washed with acetonitrile (5 mL) (14.5 mg, 21% yield based upon 1-norbornyllithium). ^1H NMR (benzene-d_6, 25 °C, 400 MHz) δ: 1.08 (br s, 24H), 1.46 (br s, 8H), 1.598 (br s, 8H), 2.33 (br s, 4H).

Synthesis of $Fe(1\text{-norbornyl})_4$ from $Fe(acac)_3$. To a cold (−25 °C) stirring solution of 1-norbornyllithium (51.8 mg, 0.51 mmol) in pentane (10 mL) was added $Fe(acac)_3$ (44.0 mg, 0.12 mmol). This was allowed to stir for 3 h, during which time the solution darkened and a white solid was deposited. The mixture was filtered through a basic alumina column supported on glass wool (0.5 × 4 cm). The vibrant purple filtrate was dried in vacuo, and the purple solid was washed with acetonitrile (5 mL) (11.5 mg, 21% yield based upon 1-norbornyllithium). ^1H NMR (benzene-d_6, 25 °C, 400 MHz) δ: 1.08 (br s, 24H), 1.46 (br s, 8H), 1.60 (br s, 8H), 2.33 (br s, 4H).

Synthesis of $[Li(12\text{-crown-}4)_2][Fe(N=C^tBu_2)_4]$ (5). To a brown solution of $[Li(DME)][Fe(N=C^tBu_2)_4]$ (115.3 mg, 0.16 mmol) in Et_2O (2 mL) was added a solution of 12-crown-4 (65.4 mg, 0.37 mmol) in pentane (3 mL). Storage of the resulting solution at −25 °C for 24 h resulted in the deposition of a maroon solid, which was isolated by decanting off the supernatant (132.0 mg, 84% yield). Anal. Calcd for $FeN_4C_{52}H_{104}O_8Li$: C, 63.98; H, 10.74; N, 5.74. Found: C, 63.77; H, 11.02; N, 5.64. ^1H NMR (pyridine-d_5, −36 °C, 500 MHz) δ: 31.1 (br s), 3.67 (s, 12-crown-4). $^7Li\{^1H\}$ NMR (pyridine-d_5, −36 °C, 500 MHz) δ: 3.4 (br s). ^1H NMR (pyridine-d_5, −28 °C, 500 MHz) δ: 57.0 (br s), 45.4 (br s), 30.9 (br s), 3.67 (s, 12-crown-4). $^7Li\{^1H\}$ NMR (pyridine-d_5, −28 °C, 500 MHz) δ: 3.4 (br s). ^1H NMR (pyridine-d_5, −20 °C, 500 MHz) δ: 55.0 (br s), 45.3 (br s), 30.6 (br s), 3.67 (s, 12-crown-4). $^7Li\{^1H\}$ NMR (pyridine-d_5, −20 °C, 500 MHz) δ: 3.4 (br s). ^1H NMR (pyridine-d_5, −3 °C, 500 MHz) δ: 51.7 (br s), 41.5 (br s), 30.0 (br s), 3.67 (s, 12-crown-4). $^7Li\{^1H\}$ NMR (pyridine-d_5, −3 °C, 500 MHz) δ: 3.3 (br s). ^1H NMR (pyridine-d_5, 11 °C, 500 MHz) δ: 49.3 (br s), 39.7 (br s), 29.4 (br s), 3.66 (s, 12-crown-4). $^7Li\{^1H\}$ NMR (pyridine-d_5, 11 °C, 500 MHz) δ: 3.2 (br s). ^1H NMR (pyridine-d_5, 25 °C, 500 MHz) δ: 46.9 (br s), 37.8 (br s), 28.7 (br s), 3.66 (s, 12-crown-4). $^7Li\{^1H\}$ NMR (pyridine-d_5, 25 °C, 500 MHz) δ: 3.2 (br s). ^1H NMR (pyridine-d_5, 42 °C, 500 MHz) δ: 44.5 (br s), 35.9 (br s), 28.0 (br s), 3.66 (s, 12-crown-4). $^7Li\{^1H\}$ NMR (pyridine-d_5, 42 °C, 500 MHz) δ: 3.2 (br s). UV−vis (C_4H_8O, 7.05×10^{-5} M): 480 nm (ε = 3237 L mol^{-1} cm^{-1}). IR (KBr, cm^{-1}): 1650 (s, ν(N=C)), 1620 (m, ν(N=C)), 1479 (s), 1444 (m), 1387 (m), 1360 (s), 1302 (w), 1288 (m), 1246 (m), 1203 (s), 1136 (s), 1093 (s), 1022 (s), 945 (m), 924 (br, m), 916 (s), 843 (s), 552 (m), 484 (m).

X-ray Crystallography. Data for **3** and **4** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (α = 0.71073 Å). The crystals of **3** and **4** were mounted on a cryoloop under Paratone-N oil, and the data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. Data for **5** were collected on a Bruker 3-axis platform diffractometer equipped with a SMART-1000 CCD detector using a graphite monochromator with a Mo Kα X-ray source (α = 0.71073 Å). The crystal of **5** was mounted on a glass fiber under Paratone-N oil, and data were collected at 150(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω-scans with 0.5° frame widths for **3** and **4** and 0.3° frame widths for **5**. Frame exposures of 25 and 10 s were used for **3** and **5**, respectively, while frame exposures of 5 s (low angle) and 15 s (high angle) were used for **4**. Data collection and cell parameter determinations were conducted using the SMART program.[60] Integration of the data frames and final cell parameter refinements were performed using SAINT software.[61] Absorption correction of the data for **3** and **4** was carried out using the multiscan method SADABS,[62] while the absorption correction of the data for **5** was carried out empirically based on reflection ψ-scans. Subsequent calculations were carried out using SHELXTL.[63] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[63]

Complex **4** exhibits positional disorder about each quaternary carbon bound to iron. Alternate positions for the 1-norbornyl groups were not assigned. Only the iron center and the α-carbon atoms were refined anisotropically. Idealized hydrogen atoms were not assigned to the isotropic carbon atoms. A summary of the relevant crystallographic data for **3**−**5** are presented in Table 2.

Table 2. X-ray Crystallographic Data for Complexes 3−5

	3	4	5
empirical formula	$FeN_2C_{23}O_2H_{43}$	$FeC_{28}H_{44}$	$FeN_4C_{52}H_{104}O_8Li$
crystal habit, color	block, purple	block, purple	block, maroon
crystal size (mm)	0.40 × 0.10 × 0.05	0.40 × 0.40 × 0.10	0.60 × 0.50 × 0.40
crystal system	triclinic	orthorhombic	monoclinic
space group	$P\overline{1}$	$Pmn2_1$	$C2/c$
vol (Å^3)	1247.52(13)	1160.91(8)	5982(3)
a (Å)	8.4491(5)	11.7710(5)	19.260(6)
b (Å)	11.0002(6)	10.0996(4)	19.428(6)
c (Å)	15.0329(9)	9.7652(4)	16.840(6)
α (deg)	68.873(4)	90.00	90.00
β (deg)	84.357(4)	90.00	108.316(6)
γ (deg)	73.185(4)	90.00	90.00
Z	2	2	4
fw (g/mol)	435.44	436.48	976.18
density (calcd) (Mg/m^3)	1.159	1.249	1.084
abs coeff (mm^{-1})	0.623	0.661	0.300
F_{000}	474.00	476	2148
total no. of reflections	10797	13440	19556
no. of unique reflections	4265	1902	4368
R_{int}	0.0260	0.0222	0.1438
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0312 wR_2 = 0.0767	R_1 = 0.1339 wR_2 = 0.3659	R_1 = 0.0755 wR_2 = 0.2000
largest diff peak and hole (e$^-$ Å^{-3})	0.284 and −0.250	2.461 and −0.791	0.628 and −0.463
GOF	1.020	1.113	1.175

■ ASSOCIATED CONTENT

S Supporting Information

X-ray crystallographic details (as CIF files) and spectral data for complexes **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Email: hayton@chem.ucsb.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation (NSF) (CHE 1059097) and Alfred P. Sloan Foundation for financial support of this work. The research carried out here made use of the SQUID Magnetometer at the Materials Research Laboratory, an NSF Materials Research Science and Engineering Center, supported by NSF Grant DMR 1121053. We also thank Prof. Paul Chirik for helpful discussions.

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