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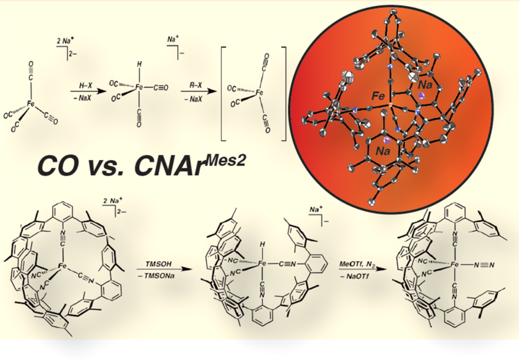
Synthesis and Protonation of an Encumbered Iron Tetraisocyanide Dianion

Charles C. Mokhtarzadeh, Grant W. Margulieux, Alex E. Carpenter, Nils Weidemann, Curtis E. Moore, Arnold L. Rheingold, and Joshua S. Figueroa*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive Mail Code 0358, La Jolla California 92093-0358, United States

Ⓢ *Supporting Information*



ABSTRACT: Reported here are synthetic studies probing highly reduced iron centers in an encumbering tetraisocyano ligand environment. Treatment of $FeCl_2$ with sodium amalgam in the presence of 2 equiv of the *m*-terphenyl isocyanide $CNAr^{Mes2}$ (Ar^{Mes2} = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) produces the disodium tetraisocyanoferrate $Na_2[Fe(CNAr^{Mes2})_4]$. Structural characterization of $Na_2[Fe(CNAr^{Mes2})_4]$ revealed a tight ion pair, with the Fe center adopting a tetrahedral coordination geometry consistent with a d^{10} metal center. Attempts to disrupt the cation−anion contacts in $Na_2[Fe(CNAr^{Mes2})_4]$ with cation-sequestration reagents lead to decomposition, except for the case of 18-crown-6, where a mononuclear complex featuring a dianionic 1-azabenz[*b*]azulene ligand was isolated in low yield. Formation of this 1-azabenz[*b*]azulene is rationalized to proceed by an aza-Büchner ring expansion of a $CNAr^{Mes2}$ ligand mediated by a coordinatively unsaturated Fe center. Disodium tetraisocyanoferrate $Na_2[Fe(CNAr^{Mes2})_4]$ is readily protonated by trimethylsilanol ($HOSiMe_3$) to produce the monohydride ferrate salt, $Na[HFe(CNAr^{Mes2})_4]$, the anionic portion of which serves as an isocyano analogue of the hydrido-tetracarbonyl metalate $[HFe(CO)_4]^-$. Treatment of $Na[HFe(CNAr^{Mes2})_4]$ with methyl triflate (MeOTf; OTf = $[O_3SCF_3]^-$) at low temperature in the presence of dinitrogen yields the five-coordinate Fe(0) complex $Fe(N_2)(CNAr^{Mes2})_4$. The formation of $Fe(N_2)(CNAr^{Mes2})_4$ in this reaction is consistent with the intermediacy of the neutral tetraisocyanide $Fe(CNAr^{Mes2})_4$. The decomposition of $Fe(N_2)(CNAr^{Mes2})_4$ to the dimeric complex $[Fe(\eta^6\text{-}(Mes)\text{-}\mu^2\text{-}C\text{-}CNAr^{Mes})]_2$ and a seven-membered cyclic imine derived from a $CNAr^{Mes2}$ ligand is presented and provides insight into the ability of $CNAr^{Mes2}$ and related *m*-terphenyl isocyanides to stabilize zerovalent four-coordinate iron complexes in a strongly π-acidic ligand field.

■ INTRODUCTION

Tetracarbonylferrate(2−) ($[Fe(CO)_4]^{2-}$) is one of the most well-known and well-studied organometallic complexes.[1−5] It has been shown to mediate a host of important transformations in organic synthesis including carbonylation, reductive coupling, reduction, and nucleophilic displacement.[2,5] This inherent reactivity of $[Fe(CO)_4]^{2-}$ originates from a high-energy, closed-shell, d^{10} orbital manifold that manifests from a doubly reduced, formally Fe(2−) center. It is well-understood that π-backbonding interactions to the carbonyl ligands stabilize the excess charge equivalents on the Fe center of this dianion.[4,6] However, the degree of π-backbonding, while significant, does not preclude the Fe center from functioning readily as a nucleophile toward a wide range of electrophilic substrates.[2]

In 2007, Ellis reported the first tetraisocyano analogue of $[Fe(CO)_4]^{2-}$, namely, $[Fe(CNXyl)_4]^{2-}$ (Xyl = 2,6-$Me_2C_6H_3$),[7] and showed that it exhibits structural features and a reactivity profile toward $ClSnPh_3$ similar to that of $[Fe(CO)_4]^{2-}$.[8] This work advanced the long-standing interest in isocyanide variants of the carbonyl metalates,[9−18] which began with Cooper's synthesis of $[Co(CNXyl)_4]^-$ as an analogue of $[Co(CO)_4]^-$.[9] The impetus for generating and studying isocyanide analogues of the carbonyl metalates stems from the fact that isocyanides are excellent π-acids, but are far stronger σ-donors than carbon monoxide.[19−24] Accordingly, efforts have been made to exploit this difference in σ-donor-strength to provide a class of highly reduced organometallics that display nucleophilic character exceeding that of the homoleptic carbonyl metalates. In recent years, our group has extended the chemistry of isocyano metalates through the use of sterically encumbering *m*-terphenyl isocyanide ligands.[25−35] The goal of these investigations has been to couple the potentially increased nucleophilicity of isocyano metalates with a kinetically stabilizing steric environment. This approach has resulted in the successful synthesis of the tetraisocyano cobalt monoanion, $[Co(CNAr^{Mes2})_4]^-$ (Ar^{Mes2} = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$),[36] which retains a mononuclear formulation upon oxidation, and a highly reactive synthon for the coordinatively unsaturated trisisocyano cobalt monoanion, $[Co(CNAr^{Mes2})_3]^-$.[37]

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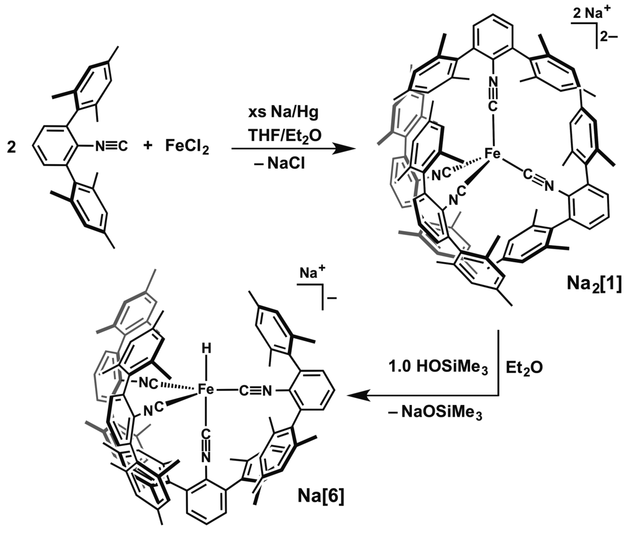
In this article, we expand our work on *m*-terphenyl isocyanide-supported metalates and present the synthesis and characterization of $[Fe(CNAr^{Mes2})_4]^{2-}$, which is a sterically encumbered variant of Ellis' dianion, $[Fe(CNXyl)_4]^{2-}$. We also demonstrate that $[Fe(CNAr^{Mes2})_4]^{2-}$ is protonated readily, leading to the reactive monohydride isocyanometalate $[HFe(CNAr^{Mes2})_4]^-$. Both $[Fe(CNAr^{Mes2})_4]^{2-}$ and $[HFe(CNAr^{Mes2})_4]^-$ display properties that parallel their well-known carbonyl analogues (i.e., $[Fe(CO)_4]^{2-}$ and $[HFe(CO)_4]^-$),[38] but also display distinct reactivity and decomposition profiles that are emblematic of a sterically encumbered isocyano environment.

■ RESULTS AND DISCUSSION

Treatment of 2 equiv of $CNAr^{Mes2}$ with $FeCl_2$ followed by the addition of sodium amalgam provides the disodium tetraisocyanoferrate salt, $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]), as a brick red crystalline solid in 23% isolated yield (Scheme 1). While the yield of $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) by this protocol is modest, the reaction can be carried out at room temperature and does not require a slow addition of reducing agent.[7] Notably, use of a higher equivalency of $CNAr^{Mes2}$ in this reaction does not lead to improved yields. Tetraisocyanoferrate $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) gives rise to a single, sharp set of Ar^{Mes2} resonances in its ^1H NMR spectrum (C_6D_6). The $^{13}C\{^1H\}$ NMR spectrum of $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) likewise displays a single Ar^{Mes2} environment and additionally features a significantly deshielded resonance at +219.2 ppm assigned to the Fe-bound isocyano carbon atoms. Notably, the large downfield $^{13}C\{^1H\}$ NMR resonance for the Fe-bound carbon atoms in $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) is consistent with those observed for both $K_2[Fe(CNXyl)_4]$ and $K_2[Fe(CO)_4]$ (238.7 and 234.6 ppm,[7] respectively) and can be considered an NMR spectroscopic marker for significant Fe-to-ligand *π*-back-donation.[15,39,40] The solution IR spectrum (C_6D_6) of $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) is also in line with this interpretation and features a broad, prominent band centered at 1682 cm^{-1} assignable to a low-energy isocyanide $\nu(CN)$ stretch. In comparison, $K_2[Fe(CNXyl)_4]$ also gives rise to a broad, low-energy $\nu(CN)$ band centered at 1670 cm^{-1} (THF).[7]

Scheme 1



Single crystals of $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) can be grown from a saturated Et_2O solution stored at −35 °C. In the solid state, $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) is found as an unsolvated contact-ion pair[41] with significant interactions between the Na cations and isocyano CN units, as well as between the Na cations and the *π*-faces of the $CNAr^{Mes2}$ mesityl rings (Figure 1). In this regard, the solid-state structure of $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) resembles that of the cobalt isocyanometalate, $Na[Co(CNAr^{Mes2})_4]$, which likewise exhibited Na/isocyano and Na/*π*-arene interactions.[36] Despite this ion pairing, however, the Fe center in $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) adopts a tetrahedral coordination geometry (Houser τ_4 geometry index[42] = 0.97) as expected for a d^{10}, four-coordinate metal center.

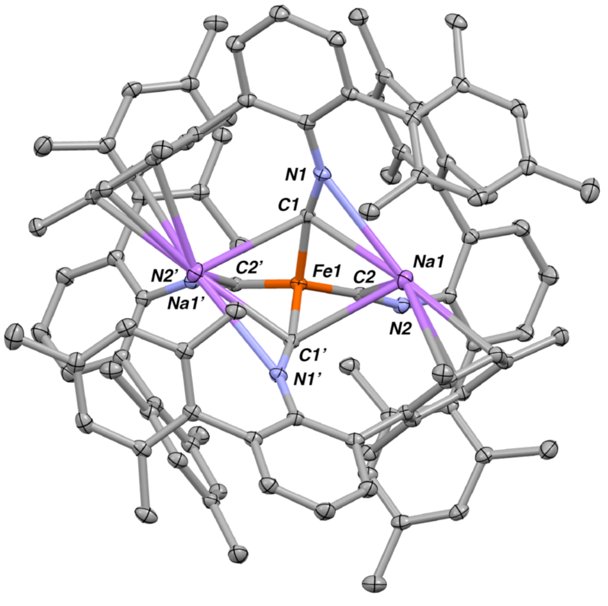


Figure 1. Molecular structure of $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]).

The metrical parameters associated with $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]) are also consistent with a substantial degree of Fe-to-isocyanide *π*-back-donation. As shown in Table 1, Na_2[**1**] exhibits very short average $Fe-C_{iso}$ bond lengths and significantly elongated average $C_{iso}-N$ bond lengths relative to the formally Fe(0) complexes $Fe(CO)_4(CNAr^{Mes2})$ (**2**) and $Fe(CO)_3(CNAr^{Mes2})_2$ (**3**), and the formally Fe(II) complex *cis,cis,trans*-$FeI_2(CO)_2(CNAr^{Mes2})_2$ (**4**) (Figure 2). However, the average $Fe-C_{iso}$ and $C_{iso}-N$ bond lengths in Na_2[**1**] are slightly longer and slightly shorter, respectively, than the

Table 1. Average $Fe-C_{iso}$ and $C_{iso}-N_{iso}$ Bond Distances for Tetraisocyano and Related Iron Complexes

compd	$d(Fe-C_{iso})_{av}$ (Å)	$d(C_{iso}-N_{iso})_{av}$ (Å)
$Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**])[a]	1.789(18)	1.219(17)
$[K(crypt\text{-}[2.2.2])]_2[Fe(CNXyl)_4]$[b]	1.765(3)	1.237(7)
$Fe(CO)_4(CNAr^{Mes2})$ (**2**)	1.869(3)	1.157(3)
$Fe(CO)_3(CNAr^{Mes2})_2$ (**3**)[a]	1.845(6)	1.160(5)
cis,cis,trans-$FeI_2(CO)_2(CNAr^{Mes2})_2$ (**4**)	1.877(2)	1.152(2)
$Na[HFe(CNAr^{Mes2})_4]$ (Na[**6**])	1.801(17)	1.208(20)
$Fe(N_2)(CNAr^{Mes2})_4$ (**7**)	1.843(20)	1.186(8)

[a] Average of two crystallographically independent molecules. [b] Ref 7.

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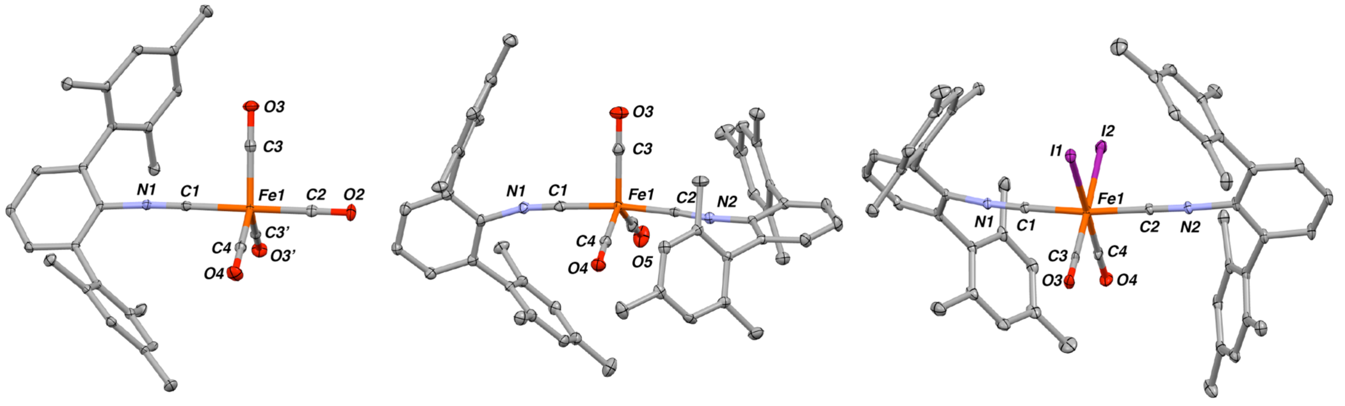

Figure 2. Molecular structures of $Fe(CO)_4(CNAr^{Mes2})$ (**2**, left), $Fe(CO)_3(CNAr^{Mes2})_2$ (**3**, center), and *cis,cis,trans*-$FeI_2(CO)_2(CNAr^{Mes2})_2$ (**4**, right).

corresponding parameters found in Ellis' discrete dianion $[Fe(CNXyl)_4]^{2-}$, isolated as its di-[K-[2.2.2]cryptand)]$^+$ salt (Table 1).[7] We believe these small differences arise from the steric constraints placed on the $[Fe(CNR)_4]^{2-}$ core by both the *m*-terphenyl groups and the tightly bound sodium cations, rather than an electronic difference between the aryl isocyanides $CNAr^{Mes2}$ and CNXyl. Indeed, we have recently shown that $CNAr^{Mes2}$ and CNXyl exert a nearly identical electronic influence on metal centers, despite the presence of encumbering *ortho*-mesityl substituents in the former.[24]

In contrast to $K_2[Fe(CNXyl)_4]$,[7] disruption of the cation−anion interactions in $Na_2[\mathbf{1}]$ with cryptands or crown ethers does not provide a discrete example of $[Fe(CNAr^{Mes2})_4]^{2-}$. Several attempts to encapsulate the Na cations in $Na_2[\mathbf{1}]$ with 15-crown-5 or dibenzo-18-crown-6 in THF or Et_2O solution led to intractable mixtures, with free $CNAr^{Mes2}$ being the dominant product. These observations mirror those made for the cobaltate salt $Na[Co(CNAr^{Mes2})_4]$, for which Na−anion interactions can only be disrupted when "coordinating" cations are employed.[36,37] In addition, other highly reduced carbonyl metalates are known to decompose upon attempts to separate contact alkali-metal cation/anion pairs.[4] However, when $Na_2[\mathbf{1}]$ was treated with 2.0 equiv of 18-crown-6 (18-c-6), the bis-isocyanide cycloheptatrienyl product **5** (Figure 3) was isolated in very low yield (ca. 2%) as red-brown single crystals. The remainder of the reaction mixture contained free $CNAr^{Mes2}$ and several other decomposition products as assayed by ^1H NMR spectroscopy. Whereas the low isolated yield prevented full characterization by spectroscopic techniques, it is notable that complex **5** is formally an Fe(I) species reminiscent of the unstable metalloradical $CpFe(CO)_2$.[43] In addition, it is important to note that the η^5-cycloheptatrienyl unit in **5** is part of a formally dianionic 1-azabenz[*b*]azulene formed from an apparent aza-Büchner ring expansion of a $CNAr^{Mes2}$ ligand.[44−46] While the mechanistic sequence leading to the formation of complex **5** is presently unknown, Arnold has reported a similar aza-Büchner ring expansion for $CNAr^{Mes2}$ in the presence of a highly reduced, low-coordinate zirconium center.[47] On the basis of this precedent, we presume that removal of a Na cation from $Na_2[\mathbf{1}]$ by 18-c-6 may allow for $CNAr^{Mes2}$ dissociation and formation of a low-coordinate ferrate that is capable of inducing an aza-Büchner expansion by initial coordination of a flanking mesityl ring. In this respect, the chemistry of $Na_2[\mathbf{1}]$ may mirror that of the tetra-isocyano cobaltate salt $Na[Co(CNAr^{Mes2})_4]^-$, which has been shown to yield an equivalent of three-coordinate $[Co(CNAr^{Mes2})_3]^-$ via $CNAr^{Mes2}$ dissociation when its cation/anion contacts are disrupted.[36,37]

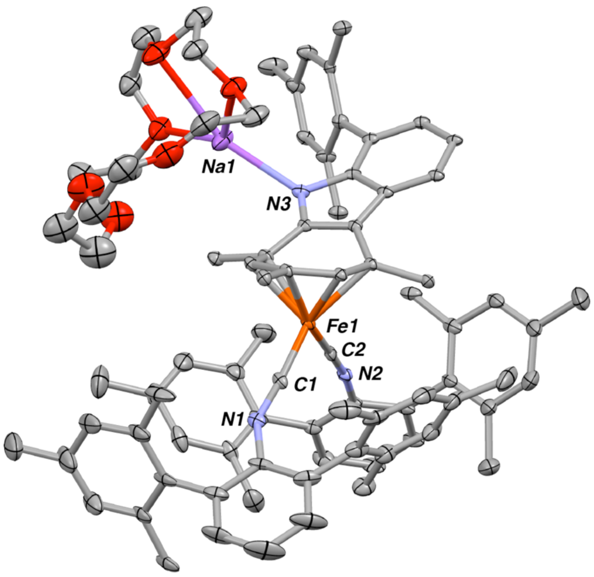

Figure 3. Molecular structure of $[Na(18\text{-crown-6})][(\eta^5\text{-}Me_6\text{-}1\text{-}azabenz[b]azulene)Fe(CNAr^{Mes2})_2]$ (**5**).

While $Na_2[\mathbf{1}]$ is not well behaved in cation-encapsulation reactions, it does react with certain protic sources to yield an isocyano analogue of $Na[HFe(CO)_4]$. As shown in Scheme 1, treatment of $Na_2[\mathbf{1}]$ with trimethylsilanol ($HOSiMe_3$; $pK_a \approx 11.5$ (DMSO)[48−50]) generates the anionic monohydride complex $Na[HFe(CNAr^{Mes2})_4]$ ($Na[\mathbf{6}]$) as a red-orange crystalline solid. Notably, treatment of cold (∼−100 °C) Et_2O solutions of $Na_2[\mathbf{1}]$ with 1.0 equiv of stronger Brønsted acids, such as 3,5-dimethylbenzoic acid, pivalic acid, pyridinium chloride ([Hpy]Cl), and ethylammonium chloride ($[EtNH_3]Cl$),[51] led to complex mixtures containing unreacted starting material, free ligand, and several unidentified products. Although not conclusively observed, we presume these reactions produce the neutral dihydride complex $H_2Fe(CNAr^{Mes2})_4$, which rapidly decomposes under the conditions surveyed. In contrast however, monohydride $Na[\mathbf{6}]$ does not react with additional equivalents of $HOSiMe_3$ in Et_2O solution. Accordingly, as has been established for the tetracarbonyl monoanion $[HFe(CO)_4]^-$,[38,52] this observation indicates that tetraisocyanide $Na[\mathbf{6}]$ exhibits only moderate Brønsted basicity in nonpolar media.

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Crystallographic characterization of Na[HFe(CNAr^{Mes2})$_4$] (Na[**6**]) revealed an unsolvated contact-ion pair with interactions between the Na cation and both the mesityl (i.e., π-arene) and CN units of the CNAr^{Mes2} ligands (Figure 4).

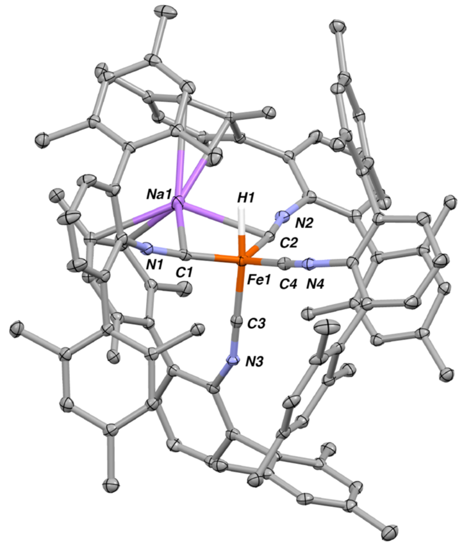
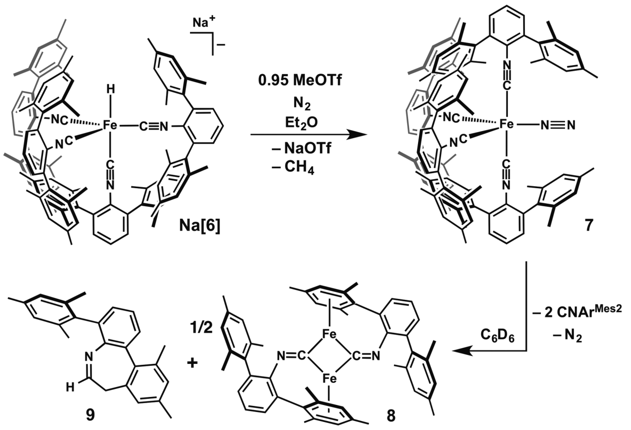


Figure 4. Molecular structure of Na[HFe(CNAr^{Mes2})$_4$] (Na[**6**]).

These contacts result in an Fe coordination geometry in the solid state that is intermediate between trigonal bipyramidal and square pyramidal on the basis of the Addison−Reedijk τ_5 geometry index (τ_5 for Na[**6**] = 0.53).[53] Nevertheless, Na[**6**] gives rise to a single set of Ar^{Mes2} resonances in its ^{1}H NMR spectrum (C_6D_6) at room temperature, thereby indicating that the [Na]$^+$/CNAr^{Mes2} contacts do not prevent a high degree of fluxionality for the five-coordinate Fe center in solution. The IR spectrum of Na[HFe(CNAr^{Mes2})$_4$] (Na[**6**]) in C_6D_6 solution displays several broad and unresolved bands in the ν(CN) stretching region, which is consistent with a lowering of the local site symmetry of either an idealized trigonal bipyramidal (C_{3v}) or square pyramidal (C_s) center by the Na cation.[54] A similar lowering of idealized site symmetry was observed in the solution IR spectrum of the related cobaltate salt Na[Co(CNAr^{Mes2})$_4$][36] and is also well-known to occur for alkali-metal salts of [HFe(CO)$_4$]$^-$ and its monophosphine derivatives (i.e., [HFe(CO)$_3$(PR$_3$)]$^-$).[54−56] However, the ν(CN) bands for Na[**6**] fall within the range 1994−1828 cm^{-1} and are markedly higher in energy that found for the dianion Na$_2$[Fe(CNAr^{Mes2})$_4$] (Na$_2$[**1**]). In addition, the Fe−C$_{iso}$ bond lengths in the solid-state structure of Na[**6**] are elongated relative to Na$_2$[**1**] (Table 1), but are significantly shorter than those found in the formally Fe(0) complexes Fe(CO)$_4$(CNAr^{Mes2}) (**2**) and Fe(CO)$_3$(CNAr^{Mes2})$_2$ (**3**). These data and comparisons indicate that the Fe center in Na[HFe(CNAr^{Mes2})$_4$] (Na[**6**]) remains highly reduced and, as is the case for [HFe(CO)$_4$]$^-$,[38] may likewise be reactive toward strong electrophiles despite exhibiting only moderate Brønsted basicity.

Scheme 2



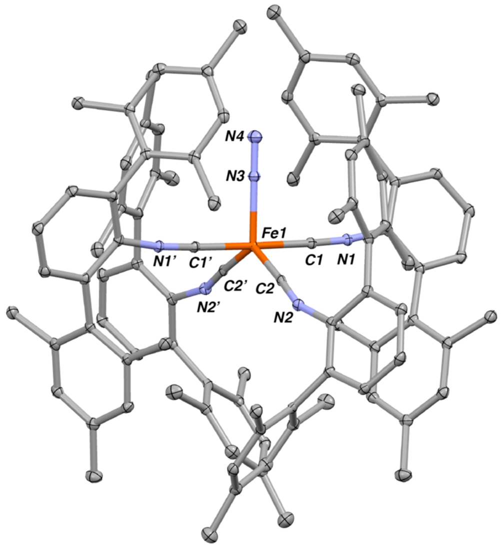


Figure 5. Molecular structure of Fe(N$_2$)(CNAr^{Mes2})$_4$ (**7**).

To test this hypothesis, Na[HFe(CNAr^{Mes2})$_4$] (Na[**6**]) was treated with methyl triflate (MeOTf; [OTf]$^-$ = [O$_3$SCF$_3$]$^-$) at −40 °C in Et$_2$O solution. This reaction proceeds readily without the buildup of detectable intermediates to yield methane (CH$_4$) and the zerovalent dinitrogen complex, Fe(N$_2$)(CNAr^{Mes2})$_4$ (**7**), as determined by both ^{1}H NMR spectroscopy and single-crystal X-ray diffraction (Scheme 2, Figure 5). In the solid state, dinitrogen complex **7** adopts a near trigonal bipyramidal coordination geometry (τ_5 = 0.86),[53] with the N$_2$ ligand located in an equatorial position. The solution IR spectrum of Fe(N$_2$)(CNAr^{Mes2})$_4$ (**7**) features a ν(NN) band centered at 2067 cm^{-1}, which is reflective of weak N≡N bond activation in the context of mononuclear Fe(0) dinitrogen complexes.[57] Most importantly however, this product outcome from the reaction between Na[**6**] and MeOTf mirrors those established by Whitmire for the reactivity of alkyl iodides with [HFe(CO)$_4$]$^-$.[58] Furthermore, in these latter studies, the unstable paramagnetic (S = 1) tetracarbonyl complex, Fe(CO)$_4$,[59−61] has been proposed as an unobservable intermediate, which then rapidly undergoes ligand redistribution and aggregation reactions. For the reaction between Na[**6**] and MeOTf, the steric encumbrance provided by the CNAr^{Mes2} ligands presumably imparts the analogous tetraisocyanide complex Fe(CNAr^{Mes2})$_4$ with a lifetime sufficient to be trapped by dinitrogen present within the reaction mixture. Notably, several isolable zerovalent FeL$_4$ complexes have now been reported.[62−64] However, none to date feature L-type ligands with two orthogonal π* orbitals akin to CO, which would render such complexes as precise electronic analogues to the high-spin, binary carbonyl Fe(CO)$_4$. In this respect, complex **7** potentially points to a molecular-design strategy for the isolation of kinetically stabilized FeL_4 complexes that more appropriately mimic the electronic features of $Fe(CO)_4$.

Thus, while the dinitrogen complex $Fe(N_2)(CNAr^{Mes2})_4$ (**7**) can be viewed as a trapped form of $Fe(CNAr^{Mes2})_4$, it is critical to note that the dissociation of N_2 from the Fe center results in a multistep decomposition process. Furthermore, this decomposition sequence highlights the points of incompatibility of the $CNAr^{Mes2}$ ligand for the goal of isolating a kinetically persistent FeL_4 species. Accordingly, when crystals of **7** are dissolved in either C_6D_6 or Et_2O at room temperature, complete conversion to the diamagnetic, symmetric dimer $[Fe(\eta^6\text{-(Mes)-}\mu^2\text{-C-}CNAr^{Mes})]_2$ (**8**) is observed over the course of *ca.* 4 h. Dimer **8** has been crystallographically characterized (Figure 6), and its solid-state structure shows that $CNAr^{Mes2}$ ligands adopt a μ^2-bridging mode, and also provide an η^6-arene interaction to the Fe centers. In this respect, dimer **8** serves as a valence-isoelectronic analogue to the neutral, bridging carbonyl dimer $[CpCo(\mu^2\text{-CO})]_2$, which has been subject to both extensive experimental and computational studies.[65−69] However, along with dimer **8**, the decomposition of $Fe(N_2)(CNAr^{Mes2})_4$ (**7**) also produces 2 equiv of free $CNAr^{Mes2}$ and the 7-membered cyclic imine **9** (Scheme 2), which was isolated from the reaction mixture and structurally characterized by X-ray diffraction (Figure 7).

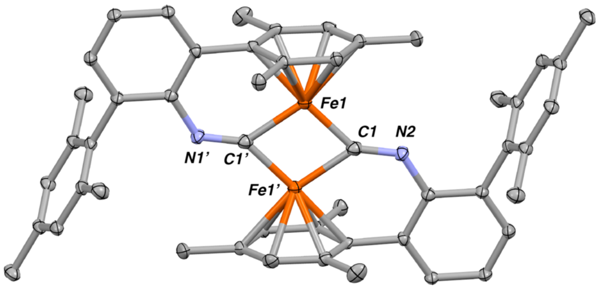


Figure 6. Molecular structure of $[Fe(\eta^6\text{-(Mes)-}\mu^2\text{-C-}CNAr^{Mes})]_2$ (**8**).

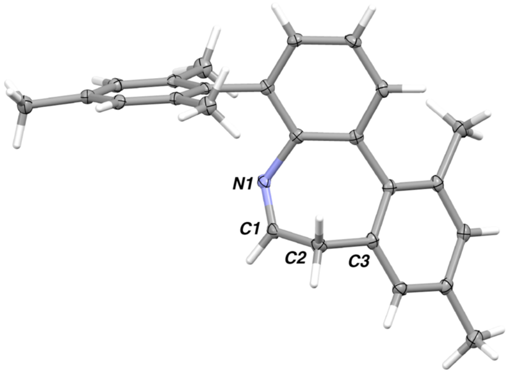


Figure 7. Molecular structure of cyclic imine (**9**).

The formation of imine **9** can be rationalized by the mechanistic sequence shown in Scheme 3, which proceeds by methyl-group C−H activation by four-coordinate $Fe(CNAr^{Mes2})_4$, followed by alkyl migration to a "tethered" isocyano unit and subsequent C−H bond reductive elimination. Notably, Jones has proposed a similar mechanism for the production of *C*-phenyl aldimines from isocyanides and benzene mediated by the related, and likewise unobservable, four-coordinate Fe species $[Fe(PMe_3)_2(CNXyl)_2]$.[70] In addition, we speculate that the driving force for the production of dimer **8** in this reaction stems from the formation of a strong η^6-arene interaction as a means to provide a coordinatively saturated Fe center. Formation of flanking-ring η^6-arene interactions from *m*-terphenyl isocyanides in this fashion is reminiscent of our previous studies on the *in-situ*-generation of three-coordinate Co and Mo isocyanide complexes.[35,37] Most importantly however, this reaction indicates that the $CNAr^{Mes2}$ framework, although seemingly able to extend the lifetime of putative $Fe(CNAr^{Mes2})_4$, is not resistant to degradation processes and secondary binding interactions by a low-coordinate Fe(0) center. Therefore, an alternative isocyanide architecture that is not susceptible to C−H activation or the formation of a strong η^6-arene interaction is required,[24,35] at minimum, to generate an isolable $Fe(CNR)_4$ complex and complete the series of isocyano analogues to the classic mononuclear iron carbonyls $Fe(CO)_5$,[71] $[Fe(CO)_4]^{2-}$,[7] $[HFe(CO)_4]^-$, and $Fe(CO)_4$.

■ CONCLUSIONS

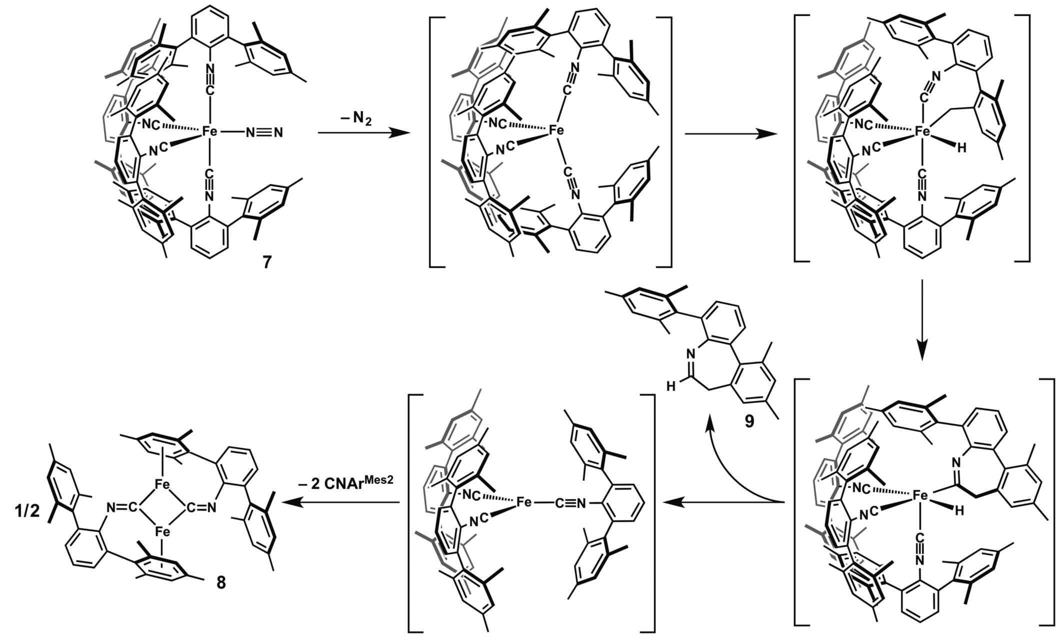
Isocyano analogues of the classic carbonyl metalates remain intriguing synthetic targets to explore the effect of enhanced metal-based nucleophilicity within a strongly π-acidic ligand field. Coupling this electronic environment with a sterically encumbering ligand topology potentially offers the ability to further control or augment the reactivity of highly reduced metal centers toward substrate molecules in both stoichiometric and catalytic transformations. Here, we show that an encumbering *m*-terphenyl isocyanide variant of $[Fe(CO)_4]^{2-}$, namely $[Fe(CNAr^{Mes2})_4]^{2-}$, can be readily prepared and isolated as a disodium contact-ion pair. The nucleophilic character of $Na_2[Fe(CNAr^{Mes2})_4]$ has been demonstrated by its reaction with $HOSiMe_3$ to produce the monohydride monoanion $[HFe(CNAr^{Mes2})_4]^-$, which serves as a unique isocyanide analogue of $[HFe(CO)_4]^-$. The latter is also shown to react readily with MeOTf at low temperatures to produce methane and the dinitrogen complex $Fe(N_2)(CNAr^{Mes2})_4$, likely via the intermediacy of the four-coordinate Fe(0) species, $[Fe(CNAr^{Mes2})_4]$. Accordingly, this synthetic sequence illustrates a reaction chemistry for these isocyanometalates paralleling that of the classic iron carbonylmetalates. We believe the synthetic results presented here will enable further development of small-molecule activation processes at a sterically protected but nucleophilic Fe center. In addition, this work has suggested the minimum requirements necessary for an isocyanide ligand framework capable of stabilizing highly reduced Fe centers with low coordination numbers.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an atmosphere of dry dinitrogen or argon using standard Schlenk and glovebox techniques. Solvents were dried and degassed according to standard procedures.[72] The isocyanide ligand $CNAr^{Mes2}$ was prepared as previously reported.[25] Unless otherwise stated, all other materials were obtained from commercial vendors and used as received. Benzene-d_6 was dried with Na/K/benzophenone followed by distillation and storage over 4 Å molecular sieves for 3 days prior to use. Celite 405 (Fischer Scientific) was dried under vacuum for 24 h at a temperature greater than 250 °C and stored in a glovebox prior to use.

Solution ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Mercury 400 spectrometer and a Varian XSENS-500 spectrometer. ^1H and $^{13}C\{^1H\}$ chemical shifts are reported in ppm relative to $SiMe_4$ (^1H and ^{13}C δ = 0.0 ppm) with reference to residual C_6D_5H solvent

Scheme 3



references of 7.16 ppm (^{1}H) and 128.06 ppm (^{13}C) for benzene-d_6.[73] FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared either as KBr pellets or as C_6D_6 solutions injected into a Thermo-Fisher solution cell equipped with KBr windows. For solution FTIR spectra, solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to that of the sample. The following abbreviations were used for the intensities and characteristics of important IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, b = broad, vb = very broad, sh = shoulder. High-resolution mass spectrometry (HRMS) was performed using an Agilent 6230 ESI-TOFMS running in positive or negative ion mode as necessary. Photolysis experiments were performed with a 254 nm model UVGL-25 Hg lamp (UVP, Inc., Upland, CA). Combustion analyses were performed by Midwest Microlab LLC, Indianapolis, IN.

Synthesis of $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[1]). To a suspension of anhydrous $FeCl_2$ (0.607 g, 4.79 mmol, 1 equiv) in a 70:30 Et_2O/THF mixture (100 mL) was added CNAr^{Mes2} (3.08 g, 9.1 mmol, 1.9 equiv). The resultant suspension was allowed to stir for 5 min whereupon 0.9% sodium amalgam (Na/Hg) was added (Na 1.10 g, 47.9 mmol, 10 equiv; Hg 122 g). The reaction mixture was then shaken vigorously for 20 min resulting in a color change from pale yellow to deep red. After shaking, the reaction mixture was allowed to stir for an additional 1 h. The supernatant was then decanted from the Na/Hg, filtered over Celite, and evaporated to dryness. The resultant red solid was slurried in *n*-pentane (30 mL) followed by evaporation to dryness. This was repeated two additional times to desolvate the NaCl byproduct. The red solid then obtained was then extracted with C_6H_6 (40 mL), filtered over Celite, and then lyophilized under reduced pressure (~100 mTorr). This process was repeated an additional time to ensure removal of NaCl and Fe(0) byproducts. The resultant dark red solid was then crystallized at −40 °C from a layered THF/*n*-pentane (1:6) solution over the course of 2 days. The dark red crystals thereby obtained were washed with *n*-pentane (4 mL) and then dried *in vacuo.* Yield: 1.60 g, 1.1 mmol, 23%. Analytically pure crystals were obtained from storage of a layered toluene/*n*-hexane solution (10:1 v/v) at −40 °C for 3 days. ^{1}H NMR (499.8 MHz, C_6D_6, 20 °C): δ = 6.83 (t, 4H, J = 8 Hz, *p*-Ph), 6.78 (d, 8H, J = 8 Hz, *m*-Ph), 6.74 (s, 16H, *m*-Mes), 6.24 (s, 24H, *p*-C*H*$_3$ Mes), 2.24 (s, 24H, *p*-CH$_3$ Mes), 2.09 (s, 48H, *o*-C*H*$_3$ Mes) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 °C) δ = 219.2 (CNR), 140.1, 137.9, 136.8, 135.3, 134.8, 130.3, 128.4, 120.7, 21.6 (*o*-CH$_3$ Mes), 21.4 (*p*-CH$_3$ Mes) ppm. FTIR (C_6D_6, KBr windows, 25 °C): ν_{CN} = 1682 (s), 1607 (sh) cm^{-1} also 2956 (m), 2920 (m), 2872 (m), 2856 (m), 2038 (m), 2009 (m), 1567 (s), 1484 (w), 1439 (w), 1406 (s) 1377 (m), 1284 (w), 1271 (w), 1252 (w), 1223 (w), 1205 (w), 1095 (w), 1068 (w), 1034 (m), 852 (m), 754 (m), 636 (w), 571 (w) cm^{-1}. Anal. Calcd for $C_{100}H_{100}N_4Na_2Fe$: C, 82.28; H, 6.91; N, 3.84. Found C, 81.89; H, 6.87; N, 3.79.

Synthesis of $Fe(CO)_4(CNAr^{Mes2})$ (2). A 100 mL resealable ampoule was charged with C_6H_6 (5 mL) and $Fe_2(CO)_9$ (0.537 g, 1.47 mmol) and then stirred for 5 min. Solid CNAr^{Mes2} (1.00 g, 2.95 mmol, 2 equiv) was then added over the course of 5 min. The resulting mixture was refluxed for 5 days and then concentrated to a solid under reduced pressure. The solid was then extracted with *n*-pentane (40 mL) and filtered through Celite. The filtrate was then evaporated to dryness under reduced pressure. The resulting residue was dissolved in *n*-pentane (15 mL), filtered, and stored at −40 °C to afford pale yellow crystals, which were collected and dried *in vacuo*. Yield: 0.746 g, 1.47 mmol, 49.8%. ^{1}H NMR (499.8 MHz, C_6D_6, 20 °C): δ = 6.94 (t, 1H, J = 8 Hz, *p*-Ph), 6.91 (s, 4H, *m*-Mes), 6.82 (d, 2H, J = 8 Hz, *o*-Ph), 2.21 (s, 6H, *p*-C*H*$_3$ Mes), 2.02 (s, 12H, *o*-C*H*$_3$ Mes) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 20 °C): δ = 212.5 (CO), 170.6 (CNR), 139.1, 138.4, 135.5 (two peaks), 133.8, 129.5, 129.3, 129.0, 21.2 (*p*-CH$_3$ Mes), 20.1 (*o*-CH$_3$ Mes) ppm. FTIR (C_6D_6, KBr window, 25 °C): ν_{CN} = 2164 (s) cm^{-1}, ν_{CO} = 2051 (s), 1994 (vs), 1968 (vs) cm^{-1} also, 3055 (w, sh), 2975 (w), 2948 (w), 2920 (m), 2869 (w), 1614 (m), 1467 (sh), 1454 (m), 1416 (w), 1349 (w), 1330 (w), 1273 (vw), 1029 (vw), 851 (m), 813 (s), 787 (w), 757 (m), 735 (vw), 636 (s) 614 (s) cm^{-1}. Anal. Calcd For $C_{29}H_{25}NO_4Fe$: C, 68.65; H, 4.97; N, 2.76. Found: C, 68.80, H, 4.75; N, 2.77.

Synthesis of $Fe(CO)_3(CNAr^{Mes2})_2$ (3). To a 100 mL ampule equipped with a side arm gas inlet was added a THF solution of CNAr^{Mes2} (0.801 g, 2.36 mmol, 2 equiv, 40 mL) followed by $Fe(CO)_5$ (0.231 g, 1.18 mmol, 1 equiv). The ampule was sealed and irradiated (254 nm; Hg lamp) for 30 min, followed by a freeze−pump−thaw cycle (40 mTorr) to degas the headspace of the reaction mixture. This process was repeated 3 times, followed by continuous irradiation for 12 h. Analysis of an aliquot of the reaction mixture by ^{1}H NMR at this point revealed complete consumption of free CNAr^{Mes2}. The reaction mixture was then concentrated to a solid under reduced pressure and washed with *n*-pentane (3 × 10 mL), followed by subsequent evaporation to dryness. The resulting solid was then extracted with Et_2O (30 mL), filtered and the resulting solution evaporated to dryness to afford $Fe(CO)_3(CNAr^{Mes2})_2$ as a yellow solid. Yield: 0.332 g, 0.405 mmol, 34.3%. X-ray diffraction quality crystals were obtained from storage of a layered solution of THF/*n*-hexane (1:10) at room

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temperature over the course of 1 week. ^{1}H NMR (399.9 MHz, C_6D_6, 20 °C): δ = 6.91 (t, 2H, J = 8 Hz, p-Ph), 6.87 (s, 8H, m-Mes), 6.80 (d, 4H, J = 8 Hz, m-Ph), 2.22 (s, 12H, p-CH_3 Mes), 2.00 (s, 24H, o-CH_3 Mes) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 °C): δ = 212.6 (CO), 178.5 (CNR), 138.6, 137.8, 135.5, 134.3, 129.2, 128.9, 128.3, 128.2, 21.2 (p-CH_3 Mes), 20.2 (o-CH_3 Mes) ppm. FTIR (C_6D_6, KBr windows, 25 °C): ν_{CN} = 2097 (s) cm^{-1}; ν_{CO} = 1936 (s) cm^{-1} also, 3030 (w), 2958 (w), 2920 (w), 2869 (w), 1416 (w), 1356 (w), 851 (w), 755 (w), 640 (w), 606 (m), 596 (w) cm^{-1}. Anal. Calcd For $C_{53}H_{50}FeN_2O_3$: C, 77.74; H, 6.16; N, 3.42. Found: C, 77.51; H, 5.88; N, 3.51.

Synthesis of *cis,cis,trans*-$FeI_2(CO)_2(CNAr^{Mes2})_2$ (4). To a thawing THF solution of $Fe(CO)_3(CNAr^{Mes2})_2$ (**4**, 0.243 g, 0.3081 mmol, 1 equiv, 13 mL) was added an equally cold THF solution of I_2 (0.0782 g, 0.0308 mmol, 1 equiv, 2 mL). The resulting mixture was allowed to slowly warm to room temperature over the course of 45 min, whereupon it was concentrated to a solid *in vacuo*. The red/brown solid was then washed with n-pentane (3 × 5 mL) and filtered. The resulting solid was then crystallized from a layered solution of THF/n-hexane (1:10) over the course of 5 days at room temperature to yield *cis,cis,trans*-$FeI_2(CO)_2(CNAr^{Mes2})_2$ as large red/brown crystals. Yield: 0.109 g, 0.104 mmol, 34%. ^{1}H NMR (399.9 MHz, C_6D_6, 20 °C): δ = 6.90 (m, 10H, p-Ph/m-Mes), 6.75 (d, 4H, J = 8 Hz, m-Ph), 2.24 (s, 12H, p-CH_3 Mes), 2.09 (s, 24H, p-CH_3 Mes) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 °C): δ = 211.4 (CO), 157.1 (CNR), 140.6, 138.2, 135.6, 134.8, 133.7, 130.2, 129.3, 129.2 (2 peaks), 21.3 (p-CH_3 Mes), 20.5 (o-CH_3 Mes) ppm. FTIR (C_6D_6, KBr windows, 25 °C): ν_{CN} = 2168 (s), 2140 (w, sh) cm^{-1}; ν_{CO} = 2058 (s), 2020 (m) cm^{-1} also 3005 (w), 2974 (w), 2940 (w), 2919 (w), 2868 (w), 2854 (w), 1466 (w), 1416 (w), 1378 (w), 850 (w), 756 (w), 605 (w), 591 (w) cm^{-1}. Anal. Calcd for $C_{52}H_{50}FeI_2N_2O_2$: C, 59.79; H, 4.82; N, 2.68. Found: C, 59.62; H, 4.91; N, 2.67.

Isolation of [Na(18-crown-6)][(η^5-Me$_6$-1-azabenz[*b*]azulene)-Fe($CNAr^{Mes2}$)$_2$] (5). To a thawing Et_2O solution of Na_2[**1**] (0.078 g, 0.054 mmol, 1 equiv, 15 mL) was slowly added an equally cold solution of 18-crown-6 (0.028 g, 0.108 mmol, 2.0 equiv, 2 mL) over the course of 2 min. The reaction mixture was allowed to stir and warm to room temperature over the course of 1 h resulting in a color change from deep red to purple. All volatile materials were then removed under reduced pressure, and the resulting purple-brown residue was washed with n-pentane (3 × 5 mL) and dried *in vacuo*. Crystallization of the residue from a layered toluene/n-hexane mixture (7:1) at −40 °C over the course of 10 days produced a small quantity of complex **5** as red-brown X-ray diffraction quality crystals. Analysis of an aliquot of the crystallization mixture by ^{1}H NMR spectroscopy indicated the presence of several unidentifiable products. Several attempts to reproduce the synthesis and isolation of **5** were unsuccessful.

Synthesis of Na[HFe($CNAr^{Mes2}$)$_4$] (Na[6]). To a thawing Et_2O solution of $Na_2[Fe(CNAr^{Mes2})_4]$ (Na_2[**1**]; 0.213 g, 0.146 mmol, 1 equiv, 15 mL) was added $HOSiMe_3$ (0.013 g, 0.146 mmol, 1.0 equiv) via microsyringe. The reaction mixture was allowed to slowly warm to room temperature over the course of 3 h, whereupon it was evaporated to dryness. The resulting red-orange solid was then washed with n-pentane (3 × 5 mL) and then thoroughly dried *in vacuo*. The resulting red solid was then extracted with C_6H_6 (10 mL), filtered, and then lyophilized to yield a red-orange powder. Yield: 0.114 g, 0.079 mmol, 54.1%. X-ray diffraction quality crystals were obtained by storage of a saturated n-pentane solution at −40 °C for 1 week. Analytically pure crystals of Na[**6**]·(NCMe) were obtained crystallization from a 3:1 NCMe/Et_2O mixture at −40 °C over the course of 2 days. ^{1}H NMR (499.8 MHz, C_6D_6, 20 °C): δ = 6.85 (m, 28H, o-Ph + p-Ph + m-Mes), 2.25 (s, 24H, p-CH_3 Mes), 2.04 (s, 48H, o-CH_3 Mes), −10.9 (s, 1H, Fe−H) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 °C): δ = 206.1 (CNR), 137.8, 137.6, 136.2, 135.7, 134.4, 130.6, 128.8, 123.0, 21.5 (p-CH_3 Mes), 21.3 (o-CH_3 Mes) ppm. FTIR (C_6D_6, KBr windows, 25 °C): ν_{CN} = 1994 (m), 1898 (s), 1846 (s), 1828 (s) cm^{-1} also 3036 (w), 2951 (w), 2918 (m), 2854 (w), 1575 (m), 1487 (w), 1407 (m), 1271 (w), 1031 (w), 852 (m), 755 (m) cm^{-1}. Anal. Calcd for $C_{102}H_{104}N_5NaFe$ (Na[**6**]·(NCMe)): C, 82.84; H, 7.09; N, 4.74. Found: C, 83.95; H, 6.83; N, 4.80.

Synthesis of Fe(N_2)($CNAr^{Mes2}$)$_4$ (7). To a thawing Et_2O solution of $Na[HFe(CNAr^{Mes2})_4]$ (Na[**6**], 0.043 g, 0.0302 mmol, 1 equiv, 10 mL) was added an equally cold Et_2O solution of MeOTf (0.0052 g, 0.0317 mmol, 1.05 equiv, 2 mL) over the course of 1 min. Upon completion of the addition, the reaction mixture was refrozen in a cold well and then placed in a −40 °C freezer to thaw and stir for 45 min. Over this time, a deep red precipitate was formed in the reaction mixture. The suspension was then filtered and the resulting solid extracted with thawing toluene (3 mL) and concentrated to a solid under reduced pressure. The resulting solid was dissolved in a 1:1 Et_2O/toluene mixture (2 mL), filtered, and stored at −40 °C for 1 day to yield deep-red crystals of **7**. Yield: 0.010 g, 0.007 mmol, 23.0%. ^{1}H NMR analysis of these crystals was sufficient to provide characterization data of the pure material. However, due to the thermal instability of the complex even at −40 °C, ^{1}H NMR analysis of the supernatant revealed that **7** was present as a mixture with complex **8** and the cyclic-imine **9**. A separate experiment performed in a sealed J-Young tube in thawing C_6D_6 indicated the formation of methane (CH_4; δ = 0.17 ppm[73]) when analyzed by ^{1}H NMR spectroscopy. Characterization data for **7** follow. ^{1}H NMR (499.8 MHz, C_6D_6, 20 °C): δ = 6.91 (m, 16H, o-Ph + m-Ph + m-Mes), 2.30 (s, 24H, p-CH_3 Mes), 2.05 (s, 48H, o-CH_3 Mes) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 °C) δ = 139.2, 137.7, 136.9, 136,3, 131.7, 130.6, 128.8, 125.1, 21.5 (p-CH_3 Mes), 20.8 (o-CH_3 Mes) ppm; prolonged scanning did not reveal the isocyanide carbon resonance. FTIR (C_6D_6, KBr windows, 25 °C): ν_{NN} = 2067 (m) cm^{-1}; ν_{CN} = 1967 (s), 1951 (s), 2017 (m, sh) cm^{-1} also 2970 (w), 2945 (w), 2920 (w), 2848 (w), 1542 (w), 1453 (m), 1416 (w), 1377 (w), 1324 (w), 851 (w), 804 (w), 756 (w), 668 (w), 631 (w) cm^{-1}. Due to the thermal instability of **7**, satisfactory combustion analysis could not be obtained.

Isolation of [Fe(η^6-(Mes)-μ^2-*C*-$CNAr^{Mes}$)]$_2$ (8) from the Decomposition of Fe(N_2)($CNAr^{Mes2}$)$_4$ (7). Dinitrogen complex **7** was prepared as described above employing $Na[HFe(CNAr^{Mes2})_4]$ (Na[**6**]; 0.025 g, 0.018 mmol, 1 equiv) and MeOTf (0.003 g, 0.020 mmol, 1.1 equiv). The deep-red precipitate obtained was dissolved in Et_2O (5 mL) and allowed to stir for 2.5 h, resulting in the complete decomposition of **7** to a mixture of [Fe(η^6-(Mes)-μ^2-C-$CNAr^{Mes}$)]$_2$ (**8**) and the cyclic-imine **9**. Filtration of the reaction mixture through a fiberglass plug afforded a dark-gray solid. Extraction of this solid with C_6H_6 followed by filtration through Celite and evaporation to dryness *in vacuo* provided dimer **8** as a blue-green powder. Crystallization from an Et_2O solution stored at −40 °C provided single crystals suitable for X-ray diffraction. Yield: 0.004 g, 0.005 mmol, 28% (based on Na[**6**]). ^{1}H NMR (499.8 MHz, C_6D_6, 20 °C): δ = 7.40 (m, 4H, m-Ph), 7.26 (s, 4H, m-Mes), 7.21 (m, 2H, p-Ph), 4.04 (s, 4H, *meta*-(η^6-Mes), 2.59 (s, 12H, o-CH_3 Mes), 2.50 (s, 6H, p-CH_3 Mes), 2.47 (s, 6H, p-CH_3 η^6-Mes), 1.13 (s, 12H, o-CH_3 η^6-Mes) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 °C): δ = 153.5 (CNR), 140.3, 136.9, 136.8, 136.1, 135.7, 130.9, 126.8, 124.7, 124.0, 114.5, 108.3, 88.5, 87.7, 30.3, 21.6, 20.0, 17.7 ppm. FTIR (C_6D_6, KBr windows, 25 °C): ν_{CN} = 1707 (s) cm^{-1} also 2919 (w), 1542 (s), 1003 (m) cm^{-1}. Multiple attempts to obtain a satisfactory combustion analysis were unsuccessful. We attribute this observation to the presence of trace amounts of cyclic-imine **9** present in bulk samples of **8**.

Isolation of Cyclic-imine 9 from the Decomposition of Fe(N_2)($CNAr^{Mes2}$)$_4$ (7). Dinitrogen complex **7** was prepared as described above employing $Na[HFe(CNAr^{Mes2})_4]$ (Na[**6**]; 0.046 g, 0.032 mmol, 1 equiv) and MeOTf (0.006 g, 0.034 mmol, 1.05 equiv). The deep-red precipitate obtained was dissolved in Et_2O (5 mL) and allowed to stir for 2.5 h, resulting in the complete decomposition of **7** to a mixture of [Fe(η^6-(Mes)-μ^2-C-$CNAr^{Mes}$)]$_2$ (**8**) and the cyclic-imine **9**. Filtration of the reaction mixture through a fiberglass plug afforded a dark-gray solid and a brown filtrate. All volatile materials were then removed from the filtrate *in vacuo*, and the resulting residue was extracted with NCMe (3 × 5 mL). The extract was then evaporated to dryness under reduced pressure to afford **9** as an off-white solid. Note: Dimer **8** and free $CNAr^{Mes2}$ show limited solubility in NCMe. Yield: 0.002 g, 0.006 mmol, 75.0% (based on 0.25 equiv

CNAr^{Mes2} per 7). ^{1}H NMR (499.8 MHz, C_6D_6, 20 °C): δ = 7.46 (dd, 1H, J = 7 Hz, *m*-Ph), 7.41 (t, 1H, J = 5 Hz, N=C(*H*)), 7.12 (dd, 1H, J = 7 Hz, *m*-Ph), 7.05 (t, 1H, J 7 Hz, *p*-Ph), 6.96 (s, H_e, *m*-Mes), 6.95 (s, 1H, *m*-Mes), 6.85 (s, 1H, *m*-Mes), 6.52 (s, 1H, *m*-Mes), 2.71 (qd, 2H, J = 5 Hz, J = 12 Hz, CH_2), 2.36 (s, 3H, CH_3 Mes), 2.30 (s, 3H, CH_3 Mes), 2.25 (s, 3H, CH_3 Mes), 2.14 (s, 3H, CH_3 Mes), 2.00 (s, 3H, CH_3 Mes) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 °C): δ = 159.0 (*C*=N), 145.8, 139.2, 138.0, 137.1, 136.6, 136.5, 136.4, 136.3, 135.9, 133.5, 131.1, 130.7, 130.4, 129.1, 128.6, 127.5, 125.7, 123.0, 37.4, 22.1, 21.2, 21.1, 20.9, 20.6 ppm. FTIR (C_6D_6, KBr windows, 25 °C): ν_{CN} = 1613 (m) cm^{-1} also 2022 (w), 2957 (w), 2919 (w) cm^{-1}. HRMS (ESI-TOF, pos. ion; NCMe) m/z calcd for $C_{25}H_{25}N$: 340.2065. Found: 340.2054 [M + H]$^+$.

Crystallographic Structure Determinations. Single-crystal X-ray structure determinations were carried out using Bruker Platform or Kappa X-ray diffractometers equipped with Mo or Cu radiation sources (sealed tube or rotating anode), low-temperature cryostats, and CCD detectors (Bruker APEX or Bruker APEX II). All structures were solved by direct methods using SHELXS[74] and refined by full matrix least-squares procedures utilizing SHELXL[74] within the Olex2 small-molecule solution, refinement, and analysis software package.[75] Crystallographic data collection and refinement information are listed in Table S1.1 (Supporting Information). Full details of disorder modeling and structure refinement are also provided in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details on crystallographic structure determinations (pdf and cif). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00730.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jsfig@ucsd.edu.

Notes

The authors declare no competing financial interest.

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(8) In addition to [Fe(CNXyl)$_4$]$^{2-}$, Ellis' 2007 communication (ref 7) also disclosed the synthesis of [Fe(CN-*t*-Bu)$_4$]$^{2-}$, which was too thermally unstable to characterize by crystallographic or spectroscopic means. However, *in-situ*-generated [Fe(CN-*t*-Bu)$_4$]$^{2-}$ reacted with ClSnPh$_3$ at −78 °C to provide *trans*-Fe(SnPh$_3$)$_2$(CN-*t*-Bu)$_4$, thus providing reasonable evidence for its existence.

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