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Terminal Iron Carbyne Complexes Derived from Arrested CO₂ Reductive Disproportionation

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Dedication ((optional))

Abstract: The encumbered tetraisocyanide dianion, Na₂[Fe(CNAr^{Mes2})₄], reacts with two molecules of CO₂ to effect reductive disproportionation to CO and carbonate ($[CO_3]^{2-}$). When the reaction is performed in the presence of silyl triflates, reductive disproportionation is arrested via silylative esterification of a mono-CO₂ adduct. This results in the formation of four-coordinate terminal iron carbynes possessing an arylcarbamate substituent due to the direct attachment of an C(O)OSiR₃ group to an isocyanide nitrogen atom. Crystallographic, spectroscopic and computational analyses of these iron-carbon multiply-bound species reveal electronic structure properties indicative of a conformationally-locked Fe-carbyne unit.

Carbon dioxide reductive disproportionation to carbon monoxide and carbonate (CO + $[CO_3]^{2-}$) has long been investigated as a potentially useful synthetic CO₂ fixation process.^[1-11] In contrast to other CO₂ reduction processes that produce CO as feedstock,^{[12-} ^{13]} reductive disproportionation is unique in that CO₂ itself serves as the ultimate oxygen-atom acceptor en route to the production of inorganic carbonate.^[7,10,11] Many electron-rich transition metal complexes, especially those that can readily function as twoelectron reductants, have been shown to mediate stoichiometric and/or catalytic CO_2 reductive disproportionation.^[2-4,7-11] Of these complexes, highly-reduced Group 6 and 8 metal carbonyl dianions have been established as the most operationally simple CO₂ reductive disproportionation archetypes due to their production of discrete alkali or alkaline-earth metal carbonate and a volatile neutral transition-metal carbonyl upon addition of two equivalents of CO2.[3-4,7] In such reductive disproportionation schemes, the reduced carbonyl metalate salts Na₂[W(CO)₅] and Na₂[Fe(CO)₄] have been extensively examined and have been proposed to share common intermediates with respect to the activated CO₂ unit.^[7] Chief among these is a proposed dianionic metal-bound dioxycarbene (i.e. $[L_nM=C(O)_2]^{2-}$),^[14] which is thought to add a second equivalent of CO₂ to begin the O-atom transfer process.^[4,7] However, due to the highly-reduced and sterically unencumbered nature of these carbonyl complexes, such intermediates have not been spectroscopically or structurally authenticated.

Recently we reported the disodium tetraisocyanoferrate(2–), Na₂[Fe(CNAr^{Mes2})₄] (Na₂[1]; Ar^{Mes2} = 2,6-(2,4,6-

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 $Me_{3}C_{6}H_{2})_{2}C_{6}H_{3}$,^[15] as an encumbered analogue of $Na_{2}[Fe(CO)_{4}]$ by virtue of possessing four *m*-terphenyl isocyanide ligands.^[16-18] We reasoned that the large steric profile provided by four ${\rm CNAr}^{{\rm Mes}2}$ ligands in this ${\rm system}^{[19\cdot21]}$ might allow for the stabilization and/or kinetic trapping of key intermediates in CO2 reductive disproportionation by a formally dianionic Fe center.^[15] Accordingly, herein, we show that Na₂[Fe(CNAr^{Mes2})₄] is indeed effective at mediating CO₂ reductive disproportionation. However, in the presence of silvl electrophiles, the initial CO₂ adduct in this process can be trapped by formal addition to isocyanide, affording unique examples of four-coordinate iron terminal carbyne complexes. These carbynes possess structural and electronic suggesting the terminal carbyne features ligand is conformationally locked into a three-fold, equatorial plane when multi-dentate ligands are absent from the system. In addition, this work highlights the beneficial secondary-reactivity patterns available to isocyanide ligands in highly-reduced environments and provides a contrast to CO₂ reductive disproportion systems featuring homoleptic carbonyl coordination spheres.[3-4,7]

Exposure of a THF solution of Na₂[Fe(CNAr^{Mes2})₄] (Na₂[1]) to an excess of CO₂ (1 atm) resulted in a rapid color change from dark red to dark orange (Scheme 1). Analysis of the reaction mixture by ¹H NMR spectroscopy indicated the clean production of a new diamagnetic species with a single CNAr^{Mes2} environment. Crystallographic structure determination revealed this product to be the five-coordinate monocarbonyl species Fe(CO)(CNAr^{Mes2})₄ (2; Figure S4.1), which is isostructural to the mono-dinitrogen complex Fe(N₂)(CNAr^{Mes2})₄.^[15] Conversion of Na₂[1] to monocarbonyl 2 indicated that a CO₂ reductive disproportionation process is likely operative, as the analogous reaction between two equivalents of CO2 and Na2[Fe(CO)4] produces Fe(CO)5 as the exclusive iron-containing product.^[3-7] Treatment of Na₂[1] with an excess of isotopically labeled ¹³CO₂ followed by analysis of **2** by ¹³C{¹H} NMR spectroscopy confirmed that the ¹³C-label was incorporated exclusively into the Fe-bound carbonyl position. This result also suggests that [O]-for-[NAr^{Mes2}] metathetical exchange, as is known to take place upon reaction of some homoleptic isocyanide complexes with CO2,[22] is not operative. In addition, extraction of this reaction mixture with alkaline D2O followed by ¹³C{¹H} NMR spectroscopic analysis revealed a single intense peak at 169 ppm,^[23] which is indicative of $[CO_3]^{2-}$ and an overall CO₂ reductive disproportionation process (Figure S1.1). It is also noteworthy that treatment of Na₂[1] with 1.0 equiv of CO₂ results in a 1:1 mixture of monocarbonyl 2 and unreacted Na₂[1], as determined by ¹H NMR spectroscopy. This product distribution indicates that the reaction between a mono-CO₂/Fe intermediate and a second equivalent of CO2 occurs at a rate

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Scheme 1. Carbon dioxide reductive disproportionation mediated by $Na_2[1]$ and proposed intermediates.

greater than that between Na₂[1] and CO₂.

Given these observations and the steric profile of Na₂[1], we reasoned that an intermediate Fe/mono-CO2 adduct could be trapped by a substrate with greater electrophilicity than that of another CO₂ molecule. Previously, it has been shown that tetraisocyanide Na₂[1], and its monoanionic derivatives, display Fe-based nucleophilicity toward both protic and electrophilic methylating reagents.^[15] However, we found that trimethylsilyl triflate (Me₃SiOTf; OTf = O_3SCF_3) does not react with this salt at room temperature in toluene solution. While we attribute this finding to the inaccessibility of the Fe center in Na₂[1] to encumbered silyl reagents, such reagents were considered an appropriate choice to potentially intercept a nucleophilic, metalbound CO₂ intermediate. Accordingly, treatment of a 1:1 mixture of Na₂[1] and Me₃SiOTf with an excess of CO₂ resulted in the $\label{eq:contact-ion} \begin{array}{lll} \mbox{formation} & \mbox{of} & \mbox{the red-orange contact-ion pair}, \\ Na[Fe=CN((Ar^{Mes2})(C(O)OSiMe_3))(CNAr^{Mes2})_3] \ (Na[\textbf{3}]; \ Scheme \ 2), \end{array}$ as determined by X-ray crystallographic analysis (Figure 1). Most importantly, four-coordinate Na[3] is best described as an arylcarbamate-substituted iron terminal carbyne and formally results from silvlative trapping of a molecule of CO2 on an isocyano nitrogen atom followed by electronic rearrangement. Notably, only three iron terminal-carbyne complexes have been reported previously^[24-26] despite their long-standing implications for homogeneous Fischer-Tropsch-type reactions.^{[2}

There are several noteworthy structural features of the terminal carbyne complex Na[3]. The Fe-C bond distance to the carbamate-carbyne unit is 1.658(10) Å (Fe1-C1) and is indicative of significant multiple-bond character. Indeed, this Fe-C distance in Na[3] is similar to that found in the five-coordinate carbyne complex (SiP₃)Fe(COSiMe₃) (d(Fe=C) = 1.671(2) Å; SiP₃ = [Si(o- $(i-Pr)_2PC_6H_4)_3$,^[25] and those found in the four-coordinate dicarbyne (DPB)Fe(COSiMe₃)₂ (d(Fe=C) = 1.639 Å and 1.676 Å; DPB = PhB(o-(i-Pr)₂PC₆H₄)₂),^[26] which were both prepared by Peters and co-workers. However, the Fe-carbyne distance in Na[3] is significantly shorter than that of the five-coordinate terminal Fe aminocarbyne cation, [Fe(CN(i-Pr)₂)(CO)₃(PPh₃)]⁺ $((d(Fe=C) = 1.734(6) \text{ Å}) \text{ prepared by Fischer.}^{(24)} \text{ In the latter}$ complex, π -donation from the diisopropylamino group to the carbyne carbon atom, which is reflected by a Ccarbyne-N bond distance of 1.267(6) Å, was proposed as the electronic origin for partial eradication of the Fe-C triple bond. Consequently the Fe-Ccarbyne bond in this cation more closely matched iron terminal carbene complexes (*i.e.* L_n Fe=CR₂).^[24] Such π -donor interactions are not present to a significant extent in Peter's alkoxy-substituted Fe



Scheme 2. Synthesis of the terminal carbyne Na[3].



Figure 1. Full molecular structure of terminal carbyne Na[3] (left). Alternate view of the primary coordination sphere of Na[3] with the *m*-terphenyl periphery in wireframe (right). Thermal ellipsoids are drawn at the 30 % probability level.^[44]

terminal carbynes.^[25-26] For Na[**3**], the C_{carbyne}-N bond distance of 1.448(12) Å (*i.e.* d(C1-N1)) is reflective of a single bond and indicates complete reduction of the isocyanide C=N group to which the silylated-CO₂ group was added. Additionally, the N-C bond distance in the carbamate N-C(O) unit of Na[**3**] (d(N1-C5) = 1.371(10) Å) is reflective of partial double-bond character, thereby indicating that the carbonyl group is a competitive π -acceptor relative to the carbyne carbon. Therefore, it is likely that the short Fe-C_{carbyne} bond length in Na[**3**] partially originates from the unique electronic environment provided by the carbamate-carbyne functionality.

The solid-state structure of Na[3] also reveals that the Fe center does not adopt a C_{3v} -symmetric coordination geometry with an apical carbyne unit.^[24] Rather, the geometry around the Fe center in Na[3] is best approximated as trigonal monopyramidal (Houser τ_4 Index = 0.84),^[28] with an axial CNAr^{Mes2} ligand (C4) and an equatorial set comprising two CNAr^{Mes2} ligands (C2 and C3) and the carbyne unit (C1). This overall Cs-symmetric structure follows from the fact that the sum of the angles between C1, C2 and C3 (i.e. 340.8°) lacks the degree of pyramidalization normally expected for tetrahedral-type structures. In addition, the average of three angles surrounding the C4 carbon are most acute in the structure (104.6°), which suggests an axial-type positioning relative to the other ligands. Significantly, the C_s -symmetric environment displayed by Na[3] in the solid state is retained in solution as determined by both ¹H and ¹³C{¹H} NMR spectroscopy. In the ¹H NMR spectrum of Na[3] $(C_6D_6$; Figures S1.2 and S1.3), twelve distinct chemical environments are found for the CNAr^{Mes2} methyl groups, thereby reflecting a significant reduction in symmetry from a canonical $C_{3\nu}$ form. Additionally, the $^{13}C{}^{1}H$ NMR spectrum (C₆D₆) of Na[**3**] gives rise to a 1:2:1 pattern of resonances at 225.9, 214.8 and 201.2 ppm, respectively, the most downfield of which is assigned to the $Fe=C_{carbyne}$ unit.^[24-26] When Na[3] is prepared using isotopically-enriched ¹³CNAr^{Mes2}, the 225.9 and 214.8 ppm resonances split into a triplet (²J = 5.0

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Figure 2. DFT calculated molecular orbitals for model [3m]-

Hz) and doublet of doublets (${}^{2}J = 5.0$ Hz, 2.5 Hz), respectively (Figure S1.6). This coupling pattern signifies two-bond ${}^{13}C{}^{-13}C$ coupling between the carbyne carbon and the equatorial isocyanides, in addition to coupling between the equatorial and axial CNAr^{Mes2} ligands,^[29] and suggests strongly that the low-symmetry observed for Na[3] in the solid state is an inherent feature of the system.

Given that terminal Fe carbynes are rare, we believe that the molecular structure of Na[3] reveals an important electronicstructure analogy with Fischer's original cationic example, [Fe(CN(*i*-Pr)₂)(CO)₃(PPh₃)]⁺.^[24] Five-coordinate [Fe(CN(j- $Pr_{2}(CO)_{3}(PPh_{3})^{\dagger}$ adopts a trigonal bipyramidal structure with an axial phosphine ligand and an equatorial carbyne. Accordingly, four-coordinate Na[3] can be viewed straightforwardly as an analogue of [Fe(CN(*i*-Pr)₂)(CO)₃(PPh₃)]⁺ stemming from removal of the axial phosphine followed by a 2e- reduction of the resulting coordination site.[30] However, geometric preservation of the remaining ligands indicates that the Fe=C triple bond of terminal Fe carbynes is configurationally locked in the equatorial plane when multi-dentate ancillaries are not present to enforce an altered relative geometry.^[25] DFT calculations on the truncated model complex [Fe=CN((Xyl)(C(O)OSiMe₃))(CNXyl)₃]⁻ ([3m]⁻; Xyl = 2,6-Me₂C₆H₃) are consistent with this notion and resulted in an optimized structure that matches the coordination geometry of Na[3] (Figure S2.1), despite lacking encumbering substituents and contact-ion pairing to the Na⁺ counterion.^[31-32] More importantly, the molecular orbitals calculated for [3m] conform to a distinctive trigonal-monopyramidal ligand field with the Fe=C triple bond located in the equatorial plane. As shown in Figure 2, the HOMO-3 and HOMO-4 calculated for $[3m]^-$ represent the π bonding framework between the Fe center and the carbyne carbon and correspond to dxz and dxy metal orbitals. The HOMO-2 calculated for $[3m]^-$ is a π -backbonding interaction between the dyz orbital and the apical isocyanide ligands, while HOMO-1 corresponds to a dx^2-y^2 component that is π -backbonding with respect to the equatorial isocyanide ligands and σ^* with respect

to the carbyne. Most significantly, the HOMO for $[3m]^-$ is Fe dz² in character and projects into the void *trans* to the apical isocyanide ligand. Such an electronic structure arrangement conforms to the classic trigonal monopyramidal splitting pattern for metal centers in π -acidic ligand fields, where dz² is the highest lying metal-based orbital.^[33] In addition, this electronic environment suggests that the addition of electrophilic substrates to a four-coordinate, carbyne anion similar to Na[3], or alternatively, addition of nucleophilic substrates to cations of the type [Fe(CR)L₃]⁺ (L = 2e⁻ donor ligand), would likely proceed to the position *cis* to the carbyne unit.



Scheme 3. Proposed mechanisms for the formation of the terminal carbyne Na[3].

With respect to the formation of carbyne Na[3], we note that intermediate species are not observed when the reaction sequence between Na₂[1], CO₂ and Me₃SiOTf is monitored by ¹H NMR spectroscopy between -50 °C and 20 °C. To date, we have been unable to determine whether CO₂ is activated and trapped on the Fe center followed by migration to the isocyanide nitrogen atom (Scheme 3, Path A), or the alternative process where activation and silylation occur directly on the isocyanide ligand (Scheme 3, Path B).^[22] We currently favor the mechanism proceeding by initial Fe-based CO₂ activation. This contention is based on the known Fe-centered reactivity of Na₂[1] with protic sources,[15] and also circumstantial evidence derived from an apparent size-dependency on silylative CO2-trapping in this system. For example, treatment of $Na_2[1]$ with CO_2 in the presence of PhMe₂SiOTf results in the corresponding carbamatecarbyne derivative. Na[Fe=CN((Ar^{Mes2})(C(O)OSiMe₂Ph))(CNAr^{Mes2})₃] (Na[4]) as the

exclusive product. However, when the more encumbering silane Ph₂MeSiOTf carbamate-carbyne, is used, the Na[Fe=CN((Ar^{Mes2})(C(O)OSiMePh₂))(CNAr^{Mes2})₃] (Na[5]) is produced in only 10% yield along with substantial quantities of the five-coordinate monocarbonyl 2. We interpret this observation as reflective of the steric profile of Ph2MeSiOTf, which renders it kinetically inefficient for trapping a mono-CO₂ adduct of Na₂[1]. It is most probable that in the absence of a silane trap, this mono-CO2 adduct reacts with another equivalent of CO2 by the traditional, metal-centered reductive disproportionation route to generate monocarbonyl 2.[3-4,7] Despite the larger steric properties associated with the silvl groups Na[4] and Na[5], both complexes exhibit structural features in the solid-state that are nearly identical to those observed for the SiMe₃-derivative, Na[3] (Figure 3; See the ESI). These findings suggest that the electronic/geometric structure correlations outlined above for Na[3] are general for this class of Fe terminal carbynes.

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Figure 3. Molecular structure of terminal carbynes Na[4] (top) and Na[5] (bottom) with the *m*-terphenyl periphery in wireframe. Thermal ellipsoids are drawn at the 30 % probability level.^[44]

We have also performed an initial screen of the reaction chemistry available to carbyne Na[3]. Notably, Na[3] does not cleanly react with protic regents with pK_a values less than *ca*. 11.5.^[34] Instead, these reagents lead to the formation of the dinitrogen complex, $Fe(N_2)(CNAr^{Mes2})_4$,^[15] as a major product through an apparent decarboxylation process. Despite the electronic structure features outlined above indicating that Na[3] should display metal-centered nucleophilic reactivity, this complex possesses several other Lewis basic sites that may interfere with such reactivity. While we are currently searching for conditions where electrophiles can cleanly add to the Fe center, it is notable that monoanions of the type, $[HFeL_4]^{-,[35-39]}$ to which carbamate-carbyne Na[3] is related, display significantly diminished metal-based nucleophilicity relative to the corresponding $[{\sf FeL}_4]^{2-}$ dianions, $^{[40-42]}$ and therefore may not be a competitive site of electrophilic attack when other Lewis basic groups are present. However, we have found conditions where Na[3] can be decarboxylated to regenerate the tetraisocyano dianion Na₂[1] in a synthetically reversible fashion. For instance, treatment of Na[3] with 2.0 equiv of Na[HBEt₃] cleanly regenerates Na₂[1] along with the formation of trimethylsilane (HSiMe₃), as assayed by ¹H NMR spectroscopy. Quenching of this mixture with D₂O, followed by ¹³C{¹H} NMR analysis also indicated the presence of ca. 1.0 equivalent of formate anion ([HCO₂]⁻). We believe this reaction proceeds by hydride attack on the carbamate SiMe₃ group, leading to decarboxylation and reformation of Na₂[1]. In addition, the liberated CO₂ is likely then trapped by a second equivalent of Na[HBEt₃] to form a formatoborate.^[43] Indeed, the use of 1.0 equiv. of Na[HBEt₃] for this reaction results in a equimolar mixture of Na₂[1] and unreacted Na[3]. While unusual, the nucleophilic desilylation of an ester-type functionality by hydride is most plausibly enabled by the electronic saturation of the carbamate carbonyl group by π donation from nitrogen, as well as a driving force provided by the loss of CO2. Nevertheless, this reactivity profile potentially opens an avenue to redirecting CO₂ reductive disproportion away from

the production of CO and [CO₃]²⁻ using isolable Fe-C multiply bound species as intermediates. Studies aimed at exploring this potential are in progress.

Acknowledgments

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 CCDC 1552466 (2), 1552467 (Na[3]), 1552468 (Na[4]) and 1552469 (Na[5]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Constellarscenario. [44] Crystallographic Data Centre.

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