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Communication

Dinitrogen Insertion and Cleavage by a Metal—Metal Bonded Tricobalt(I) Cluster

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ABSTRACT: Reduction of a tricobalt(II) tri(bromide) cluster supported by a tris(β -diketiminate) cyclophane results in halide loss, ligand compression, and metal-metal bond formation to yield a 48-electron Co^I₃ cluster, Co₃L^{Et/Me} (2). Upon reaction of 2 with dinitrogen, all metal-metal bonds are broken, steric conflicts are relaxed, and dinitrogen is incorporated within the internal cavity to yield a formally (μ_3 - η^1 : η^2 : η^1 -dinitrogen)tricobalt(I) complex, 3. Broken symmetry DFT calculations (PBE0/def2-tzvp/D3) support an N–N bond order of 2.1 in the bound N₂ with the calculated N–N stretching frequency (1743 cm⁻¹) comparable to the experimental value (1752 cm⁻¹). Reduction of 3 under Ar in the presence of Me₃SiBr results in N₂ scission with tris(trimethylsilyl)amine afforded in good yield.

espite decades of research on the century-old Haber-Bosch process, there remain mechanistic questions regarding the details for the bond-breaking and bond-forming steps at the catalyst surface. Proposed pathways favor dissociative adsorption of N2 by multiple metal centers working in concert to generate N-adatoms.¹⁻⁸ Given the limitations in direct observation of such steps on metal surfaces, however, reactivity studies of dinitrogen with metalmetal bonded molecular species can complement and inform on the mechanistic understanding of the heterogeneous system. However, N2 activation and cleavage by metal-metal bonded complexes remains rare with the most well characterized example being a niobium complex by Floriani and co-workers.⁹ Examples from the 3d metals are limited to work by the Mindiola and Lu groups. Mindiola and co-workers reported a Co(I)-Co(I) bonded complex, $[(PNP)Co]_2$, that reacts with N₂ to yield a μ -1,2-dinitrogen complex via a masked low-coordinate Co(I) species, (PNP)Co (Scheme 1).¹⁰ One system in which a metal-metal bonded unit is competent for N₂ reduction is the dicobalt core housed in a trisphosphino-(triamido)amine ligand, which catalyzes dinitrogen silylation to tris(trimethylsilyl)amine.¹¹ However, N₂ binding occurs solely at the apical cobalt in this system with the second metal influencing the electronic properties of the reactive center (Scheme 1).¹² Compounds in which the polynuclear metal architecture is retained yet the metal-metal bonding electrons participate in N2 activation were unknown. Herein, we report the reduction of $Co_3Br_3L^{Et/Me}$ (1) to yield a metal-metal bonded 48-electron tricobalt(I) cluster, $Co_3L^{Et/Me}$ (2). Reaction of 2 with N₂ affords the dinitrogen-bridged complex $Co_3(N_2)L^{Et/Me}(3)$ as a result of dissolution of all metal-metal bonding interactions (Scheme 1). The bound dinitrogen can be cleaved upon reduction of 3 in the presence of a proton surrogate.

Addition of 3 equiv of KC_8 to a THF solution of reddishpurple 1 under an Ar atmosphere affords $Co_3 L^{Et/Me}$, 2, in 32% isolated yield (Scheme 1, bottom). ¹H NMR spectra of 2

Scheme 1. N₂ Activation by Metal–Metal Bonded Complexes



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Figure 1. (A) Single crystal X-ray diffraction structure solution of 2 and (B) expanded view of the tricobalt core with Co, N, and C atoms are represented by magenta, blue, and gray ellipsoids at 70% probability, respectively. (C) Ball and stick representation depicting the connectivity of 3 with Co, N, and C atoms are represented by magenta, blue, and gray spheres, respectively. Solvent molecules and hydrogen atoms are omitted for clarity.

reveal a diamagnetic product with apparent D_3 symmetry in solution based on the number of resonances and the diagnostic splitting pattern for the diastereotopic $Ar-CH_2$ and $N-CH_2$ protons (Figure S1).¹³ In the solid-state structure of 2, the [Co₃] core is ligated only by the cyclophane with each cobalt center in a distorted octahedral environment (Figure 1), comprised of the NAcNAc chelate $(\angle N_L - Co - N_L = 91.0 -$ 93.0°), two Co–Co interactions, and two η^2 interactions to the arenes (Figure 1B). The asymmetric η^2 interactions in 2 (avg short and long contacts of 2.015 and 2.179 Å) result in a near eclipsed arene and $[Co_3]$ rings, contrasting the planarity of the arene rings and the more idealized staggered configuration in the arene face-capped trinuclear clusters and the $[Co_3]$ core.¹⁴ The Co^I centers in 2 significantly π -backbond to the arene π systems based on the slightly puckered arene rings and the upfield shifts of the ¹³C NMR resonances for the arene C atoms in 2 vs the free ligand (Figure S2). The ligand cavity in $\text{Co}_3 L^{\text{Et/Me}}$ (2) is compressed along the

 C_3 axis with an arene centroid-to-centroid distance of 3.89 Å more than 1.7 Å shorter than that observed crystallographically for any other trimetallic complex of this ligand (Table S1). This compression is achieved by a twisting of the arene caps to a staggered conformation and an acute dihedral angle of 27.69° between the plane of the NAcNAc arms and the $[Co_3]$ core. The calculated Co-Co formal shortness ratio of 1.12 based on the Co-Co distances is not suggestive of a Co-Co single bond (Figure 1B); however, Co-Co bonds of 2.6-2.7 Å have been purported by DFT methods, and $Co_3 L^{Et/Me}$ is diamagnetic at room temperature, consistent with a saturated cluster.15-23 To support this assertion, electronic structure calculations were performed on 2 at the PBE0/def2-tzvp/D3 level of theory and assuming S = 0, which gave good agreement between experimental and calculated bond metrics (Table S9). A quantum theory of atoms in molecules (QTAIM) analysis surprisingly demonstrates that a bond path only exists between Co ions and the carbon atoms bearing the ethyl substituents (Figure 2).²⁴ Thus, a better descriptor is an η^1 -coordination mode to each Co center rather than an asymmetric η^2 mode. Both the QTAIM analysis (charge concentration at the Co-Co bond critical points) and Mayer bond order (0.4) suggest similar bonding interactions between the Co-centers and other complexes possessing strong unsupported Co-Co interactions. 11,25



Figure 2. Left: QTAIM analysis of 2, 3, and 4 depicting bond paths and bond-critical points (bright green spheres). Right: contour plot of $\nabla^2 \rho$ in the mean Co–Co–Co (for 2 and 3) or Co–N₂–Co (4) planes.

We suspected that release of the steric strain in 2 could offset the energetic cost to cleave the metal bonds and allow for cooperative substrate activation. Given that $Co_3Br_3L^{Et/Me}$ is a precatalyst for catalytic silvlation of dinitrogen as reported previously, we saturated a room temperature solution of 2 with N₂ over 36 h to yield a new paramagnetic species, $Co_3N_2L^{Et/Me}$ (3), which has D_{3h} symmetry in solution based on ¹H NMR data (Figure S4).²⁶ Complete conversion can be afforded at 70 °C after 1 h. Isotopically sensitive IR absorptions assigned as the N₂ stretching vibrations in $Co_3N_2L^{Et/Me}$ are observed at

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1717 and 1752 cm $^{-1}$ with $\Delta\nu~(^{14}N_2-^{15}N_2)$ of 55 and 57 cm $^{-1}$ in drop-cast samples.

In the molecular structure of 3, the ligand adopts a more typical conformation of complexes of this cyclophane with expanded metal-metal distances (~3.66 Å) and more obtuse N_L -Co- N_L angles of ~100° (Table S3). The Co-Co separations in 3 support cleavage of all metal-metal bonds upon encapsulation of a μ_3 - η^1 : η^2 : η^1 -dinitrogen within the internal cavity (Figure 1C). Positional disorder with respect to a minor impurity (modeled as <1%) and for the bound N₂ limits detailed discussion of the N-N bond metrics. This coordination mode is rare for a homonuclear species with only three prior reports (viz. two Ti and one Cu example).²⁷⁻²⁹ IR spectra of a degassed toluene solution of 3 synthesized using $^{15}N_2~(3^{-15}N_2)$ remain unchanged before and after exposure to a $^{14}N_2$ atmosphere even after 3 d (Figure S6). Also, N_2 dissociation and reversion to 2 is not observed as $\text{Co}_{2}\text{N}_{2}L^{\text{Et/Me}}$ is stable to vacuum and storage under Ar. Thus, the solution D_{3h} symmetry observed for 3 in ¹H NMR spectra supports a low barrier to in-plane rotation of the N₂ ligand.

Broken symmetry DFT calculations on 3 (PBE0/def2-tzvp/ D3) were benchmarked to the molecular structure and vibrational data. Compound 3 displays a high degree of Coligand covalency with the frontier molecular orbitals exhibiting appreciable delocalization into the diketiminate chelates and backbonding between the Co ions and the N₂ ligand (Figure 2). The latter contrasts with the isostructural Cu₃ congener in which only metal-dinitrogen dispersive interactions are observed.²⁹ The apparent ground state of the compound is a triplet resulting from moderate antiferromagnetic coupling (J =-132.78 cm⁻¹) between the two cobalt centers that coordinate the N₂ ligand in an η^1 fashion. The calculated N₂ stretching mode at 1743.7 cm^{-1} agrees well with the experimental value and is consistent with a calculated Mayer bond order of 2.1. Finally, a QTAIM analysis also supports that the N₂ ligand possesses double-bond character, as the calculated Laplacian of the electron density $(\nabla^2 \rho)$ at the N–N bond critical point of -1.4228 au is similar to that for N₂H₂ ($\nabla^2 \rho = -1.4642$ au) and significantly higher than that for N₂ ($\nabla^2 \rho = -2.9764$ au).²⁹

Of relevance here are the formally diiron(I) and dicobalt(I) compounds L'MNNML' (L' = $[HC(C(CH_3)N(2,6$ $i \Pr_2 C_6 H_3)_2^{-}$ and the aforementioned $[(PNP)Co]_2(\mu$ - N_2).^{10,30,31} The Co $-\eta^2(N_2)$ in 3 compensates for the weaker π -backbonding interactions expected for cobalt(I) vs iron(I) (Table S2). Considering only the μ - η^1 : η^1 fragment of 3, the $M-N\equiv N-M$ unit is bent $(\angle_{M-N\equiv N} = 129.0(14)^{\circ}$, $134.5(15)^{\circ}$) and more acute than those reported by Tomson and Mindiola and Caulton ($\angle_{M-N\equiv N} = 155.1^{\circ}-163.2^{\circ}$).^{32,33} Bending of the M−N≡N−M fragment is expected to diminish the metal-dinitrogen π -overlap compared to the more linear mode. For example, ν_{N-N} for L'FeNNFeL' is ~200 cm⁻¹ lower in energy than that for Tomson's, and that for K₂[LFeNNFeL] in which two K⁺ cations are associated in a side-on fashion with the N₂ donor is more activated than that from Mindiola and Caulton (Table S2). Here then, we might infer that the side-on bound Co(I) is critical to the extent of activation of dinitrogen in 3. Indeed, comparisons of μ - η^2 : η^2 -N₂ vs μ - η^1 : η^1 -N₂ compounds support this assertion as does the calculated 22 kcal/mol stabilization afforded by adding a third Fe center bound $\eta^2(N_2)$ to the linear LFeNNFeL noted above.^{34,35}

A close analysis then of the occupied frontier MOs reveal a covalent $\text{Co}-\eta^2(N_2)$ interaction with significant $N(\pi^*)$ character. To quantitate the effect of this Co center, we

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modeled a complex in which a Co-diketiminate fragment was removed from 3 to afford a (μ -dinitrogen)dicobalt species 4. The two remaining Co-centers in 4 coordinate the N₂ ligand in an η^1 -fashion similar to that found in 3, rather than isomerizing to a μ - η^2 : η^2 mode, and the resulting calculated N–N stretching frequency increased to 1813.5 cm⁻¹. A commensurate change in Mayer bond order (2.6) and a decrease in $\nabla^2 \rho$ at the N–N bond critical point (-2.2571 au) are noted for 4 vs 3, confirming the substantial role the side-on interaction plays toward weakening the N₂ bond in 3. Expectedly, the contribution of the third Co here is estimated to be larger than that of side-on bound alkali cations in transition metal– N₂ species.

Computational studies of heterogeneous single-cluster catalysts and molecular species propose dinitrogen bound to three transition metal ions as on-pathway to N–N bond scission.⁸ Given this precedent and that 1 effects N₂ reduction to $N(SiMe_3)_3$,²⁶ Co₃N₂L^{Et/Me} was reduced with KC₈ and a silyl electrophile under an Ar atmosphere, yielding 0.6 equiv of $N(Me_3Si)_3$ after analysis of the acid-quenched filtrate by ¹H NMR spectroscopy (Figure S7). The N₂ donor in 3 is, therefore, primed for further activation and bond scission, supporting 2 and 3 as possible intermediates in the catalytic silylation of N₂ by 1. The complex product remains to be identified; comparison to catalytic dinitrogen silylation by the related iron compounds would suggest a nitride-bridged species.³⁶

In conclusion, the synthesis of a tricobalt cluster **2** in which the electrons in the metal-metal bonding interactions can be harnessed for the cooperative activation of dinitrogen in **3** is reported. $\text{Co}_3\text{N}_2\text{L}^{\text{Et/Me}}$ features a μ_3 - η^1 : η^2 : η^1 coordination mode for dinitrogen, drawing parallels to the bent coordination mode for N₂ in molecular and heterogeneous systems. Further studies on the mechanism of N₂ activation and functionalization in this and related systems are underway, as well as the potential of the [Co₃] cluster to activate other small molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c01840.

Experimental details, NMR spectra, IR spectra, computational details (PDF)

Accession Codes

CCDC 2062533–2062534 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Haber, F. Über Die Synthetische Gewinnung Des Ammoniaks. Angew. Chem. **1914**, 27 (62), 473–477.

(2) Bosch, C.; Mittasch, A.; Wolf, H.; Stern, G. Catalytic Agent for Use in Producing Ammonia. US1148570A, August 3, 1915.

(3) Ertl, G. Primary Steps in Catalytic Synthesis of Ammonia. J. Vac. Sci. Technol., A 1983, 1 (2), 1247–1253.

(4) Emmett, P. H.; Brunauer, S. The Adsorption of Nitrogen by Iron Synthetic Ammonia Catalysts. J. Am. Chem. Soc. **1934**, 56 (1), 35–41.

(5) Ertl, G.; Lee, S. B.; Weiss, M. Kinetics of Nitrogen Adsorption on Fe(111). Surf. Sci. **1982**, 114 (2), 515–526.

(6) Honkala, K.; Hellman, A.; Remediakis, I. N.; Logadottir, A.; Carlsson, A.; Dahl, S.; Christensen, C. H.; Nørskov, J. K. Ammonia Synthesis from First-Principles Calculations. *Science* **2005**, 307 (5709), 555–558.

(7) Hellman, A.; Baerends, E. J.; Biczysko, M.; Bligaard, T.; Christensen, C. H.; Clary, D. C.; Dahl, S.; van Harrevelt, R.; Honkala, K.; Jonsson, H.; Kroes, G. J.; Luppi, M.; Manthe, U.; Nørskov, J. K.; Olsen, R. A.; Rossmeisl, J.; Skúlason, E.; Tautermann, C. S.; Varandas, A. J. C.; Vincent, J. K. Predicting Catalysis: Understanding Ammonia Synthesis from First-Principles Calculations. *J. Phys. Chem. B* **2006**, *110* (36), 17719–17735.

(8) Liu, J.-C.; Ma, X.-L.; Li, Y.; Wang, Y.-G.; Xiao, H.; Li, J. Heterogeneous Fe_3 Single-Cluster Catalyst for Ammonia Synthesis via an Associative Mechanism. *Nat. Commun.* **2018**, 9 (1), 1610.

(9) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. Dinitrogen Rearranging over a Metal–Oxo Surface and Cleaving to Nitride: From the End-On to the Side-On Bonding Mode, to the Stepwise Cleavage of the N \equiv N Bonds Assisted by Nb^{III}-Calix[4]Arene. J. Am. Chem. Soc. **2000**, 122 (15), 3652–3670.

(10) Fout, A. R.; Basuli, F.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. A Co_2N_2 Diamond-Core Resting State of Cobalt(I): A Three-Coordinate Co^1 Synthon Invoking an Unusual Pincer-Type Rearrangement. *Angew. Chem., Int. Ed.* **2006**, 45 (20), 3291–3295.

(11) Siedschlag, R. B.; Bernales, V.; Vogiatzis, K. D.; Planas, N.; Clouston, L. J.; Bill, E.; Gagliardi, L.; Lu, C. C. Catalytic Silylation of Dinitrogen with a Dicobalt Complex. J. Am. Chem. Soc. 2015, 137 (14), 4638–4641.

(12) Clouston, L. J.; Bernales, V.; Carlson, R. K.; Gagliardi, L.; Lu, C. C. Bimetallic Cobalt–Dinitrogen Complexes: Impact of the Supporting Metal on N_2 Activation. *Inorg. Chem.* **2015**, *54* (19), 9263–9270.

(13) Ermert, D. M.; Gordon, J. B.; Abboud, K. A.; Murray, L. J. Synthesis of Trinuclear Tin(II), Germanium(II), and Aluminum(III) Cyclophane Complexes. *Organometallics* **2016**, *35* (21), 3651–3657.

(14) Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G. Arene Clusters. *Chem. Rev.* **1994**, *94* (6), 1585–1620.

(15) Cotton, F. A. Chromium Compounds. In *Multiple Bonds between Metal Atoms*, 3rd ed.; Cotton, F. A., Murillo, C. A., Walton, R. A., Eds.; Springer: Boston, MA, 2005; p 44.

(16) Pauling, L. Atomic Radii and Interatomic Distances in Metals. J. Am. Chem. Soc. **1947**, 69 (3), 542–553.

(17) Wade, K. The Structural Significance of the Number of Skeletal Bonding Electron-Pairs in Carboranes, the Higher Boranes and Borane Anions, and Various Transition-Metal Carbonyl Cluster Compounds. J. Chem. Soc. D 1971, 15, 792–793.

(18) Wei, C. H.; Dahl, L. F. Organometallic Sulfur Complexes. VI. Molecular Structure of a Tricyclic Complex, Tricobalt Enneacarbonyl Sulfide. *Inorg. Chem.* **1967**, *6* (6), 1229–1236.

(19) Peng, S.-M.; Liaw, D.-S.; Wang, Y.; Simon, A. Cofacial Dimer of a Diiminosuccinonitrile Complex Containing a $Co^{II}-Co^{II}$ Bond and Its Reduction to Monomeric Co^{I} Complex. *Angew. Chem., Int. Ed. Engl.* **1985**, 24 (3), 210–211.

(20) Haumann, M.; Meijboom, R.; Moss, J. R.; Roodt, A. Synthesis, Crystal Structure and Hydroformylation Activity of Triphenylphosphite Modified Cobalt Catalysts. *Dalton Trans* **2004**, *11*, 1679–1686. (21) Casati, N.; Macchi, P.; Sironi, A. Staggered to Eclipsed Conformational Rearrangement of $[Co_2(CO)_6(PPh_3)_2]$ in the Solid State: An X-Ray Diffraction Study at High Pressure and Low Temperature. *Angew. Chem., Int. Ed.* **2005**, *44* (47), 7736–7739.

(22) Brown, G. M.; Finholt, J. E.; King, R. B.; Bibber, J. W. Poly(Tertiary Phosphines and Arsines). 18. Preparation and Structure of $Bis\{\mu$ -[(Methylamino)Bis(Dimethoxyphosphine)]}-Bis-(Dicarbonylcobalt), a Binuclear Complex with Approximate Square-Pyramidal and Trigonal-Bipyramidal Coordination of Cobalt Atoms in the Same Molecule. *Inorg. Chem.* **1982**, *21* (6), 2139–2145.

(23) Karsch, H. H.; Milewski-Mahrla, B.; Besenhard, J. O.; Hofmann, P.; Stauffert, P.; Albright, T. A. Complexes with Phosphinomethanes and -Methanides as Ligands. 10. Formation, Structure, and Properties of $\{[(PMe_2CH_2PMe_2)(PMe_3)Co]_2PMe_2\}$, a Dinuclear, Odd-Electron Cobalt Complex of Formal Oxidation State Co₂+. Electronic Structure of $[CoL_3]_2PR_2$ Radicals. *Inorg. Chem.* **1986**, 25 (21), 3811–3821.

(24) Bader, R. F. W. Atoms in Molecules: A Quantum Theory; The International series of monographs on chemistry; Clarendon Press; Oxford University Press: Oxford [U.K.], New York, 1994; pp 1–458. (25) Garcia, T. Y.; Fettinger, J. C.; Olmstead, M. M.; Balch, A. L. Splendid Symmetry: Crystallization of an Unbridged Isomer of $Co_2(CO)_8$ in $Co_2(CO)_8 \cdot C_{60}$. Chem. Commun. 2009, 46, 7143–7145. (26) Eaton, M. C.; Knight, B. J.; Catalano, V. J.; Murray, L. J. Evaluating Metal Ion Identity on Catalytic Silylation of Dinitrogen Using a Series of Trimetallic Complexes. Eur. J. Inorg. Chem. 2020, 2020 (15–16), 1519–1524.

(27) Pez, G. P.; Apgar, P.; Crissey, R. K. Reactivity of $[\mu-(\eta^1:\eta^5-C_5H_4)](\eta-C_5H_5)_3\text{Ti}_2$ with Dinitrogen. Structure of a Titanium Complex with a Triply Coordinated N₂ Ligand. *J. Am. Chem. Soc.* **1982**, 104 (2), 482–490.

(28) Semproni, S. P.; Milsmann, C.; Chirik, P. J. Side-on Dinitrogen Complexes of Titanocenes with Disubstituted Cyclopentadienyl Ligands: Synthesis, Structure, and Spectroscopic Characterization. *Organometallics* **2012**, *31* (9), 3672–3682.

(29) Murray, L. J.; Weare, W. W.; Shearer, J.; Mitchell, A. D.; Abboud, K. A. Isolation of a (Dinitrogen)Tricopper(I) Complex. J. Am. Chem. Soc. **2014**, 136 (39), 13502–13505.

(30) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. Stepwise Reduction of Dinitrogen Bond Order by a Low-Coordinate Iron Complex. *J. Am. Chem. Soc.* **2001**, *123* (37), 9222–9223.

(31) Ding, K.; Pierpont, A. W.; Brennessel, W. W.; Lukat-Rodgers, G.; Rodgers, K. R.; Cundari, T. R.; Bill, E.; Holland, P. L. Cobalt-

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Dinitrogen Complexes with Weakened N-N Bonds. J. Am. Chem. Soc. 2009, 131 (27), 9471-9472.

(32) Liu, T.; Gau, M. R.; Tomson, N. C. Mimicking the Constrained Geometry of a Nitrogen-Fixation Intermediate. *J. Am. Chem. Soc.* **2020**, 142 (18), 8142–8146.

(33) Sorsche, D.; Miehlich, M. E.; Searles, K.; Gouget, G.; Zolnhofer, E. M.; Fortier, S.; Chen, C.-H.; Gau, M.; Carroll, P. J.; Murray, C. B.; Caulton, K. G.; Khusniyarov, M. M.; Meyer, K.; Mindiola, D. J. Unusual Dinitrogen Binding and Electron Storage in Dinuclear Iron Complexes. J. Am. Chem. Soc. **2020**, 142 (18), 8147–8159.

(34) Singh, D.; Buratto, W. R.; Torres, J. F.; Murray, L. J. Activation of Dinitrogen by Polynuclear Metal Complexes. *Chem. Rev.* **2020**, *120* (12), 5517–5581.

(35) Figg, T. M.; Holland, P. L.; Cundari, T. R. Cooperativity Between Low-Valent Iron and Potassium Promoters in Dinitrogen Fixation. *Inorg. Chem.* **2012**, *51* (14), 7546–7550.

(36) Ferreira, R. B.; Cook, B. J.; Knight, B. J.; Catalano, V. J.; García-Serres, R.; Murray, L. J. Catalytic Silylation of Dinitrogen by a Family of Triiron Complexes. *ACS Catal.* **2018**, *8* (8), 7208–7212.