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Strong π-Backbonding Enables Record Magnetic Exchange Coupling Through Cyanide

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Supporting Information

ABSTRACT: The paramagnetic cyano-bridged complex $PhB(^tBuIm)_3Fe-NC-Mo(N^tBuAr)_3$ (Ar = 3,5-$Me_2C_6H_3$) is readily assembled from a new four-coordinate, high-spin (S = 2) iron(II) monocyanide complex and the three-coordinate molybdenum(III) complex $Mo(N^tBuAr)_3$. X-ray diffraction and IR spectroscopy reveal that delocalization of unpaired electron density into the cyanide π* orbitals leads to a reduction of the C−N bond order. Direct current (dc) magnetic susceptibility measurements, supported by electronic structure calculations, demonstrate the presence of strong antiferromagnetic exchange between spin centers, with a coupling constant of $J = -122(2)$ cm^{-1}. To our knowledge, this value represents the strongest magnetic exchange coupling ever to be observed through cyanide. These results demonstrate the ability of low-coordinate metal fragments to engender extremely strong magnetic exchange coupling through cyanide by virtue of significant π-backbonding into the cyanide ligand.

Owing to its strong directionality and predictable binding modes, the cyanide ligand has found tremendous utility as a bridging ligand in the directed synthesis of magnetic solids and clusters.[1] For instance, the past several decades have seen the realization of metal−cyanide-based bulk magnets,[2] one-dimensional single-chain magnets,[3] and discrete single-molecule magnets.[4] Nevertheless, despite the exquisite programmability and adjustability afforded by the cyanide bridge, a key limitation in the construction of these compounds is the typically weak magnetic superexchange interactions mediated through cyanide. Indeed, the maximization of coupling strength is paramount in the synthesis of molecule-based magnetic materials, as the operating temperatures of bulk magnets,[5] single-chain magnets,[3b,6] and single-molecule magnets are all directly correlated to the strength of magnetic coupling between paramagnetic centers.[7]

One strategy toward increasing the exchange coupling through cyanide involves using complexes of low-valent, early transition metals, whose relatively diffuse d orbitals facilitate more efficient overlap with the appropriate orbitals on cyanide. Along these lines, cyano-bridged complexes with the strongest magnetic exchange are typically based on electron-rich metal ions such as vanadium(II) or molybdenum(III).[8] In principle, this effect should be even further enhanced through incorporation of strongly π-backbonding paramagnetic metal fragments, which can serve to delocalize unpaired electron density onto the cyanide ligand,[9] consequently enhancing the magnetic coupling.

Toward this end, we drew inspiration from the well-developed transition metal chemistry of N_2. Despite its negative electron affinity,[10] strongly π-backbonding metal fragments are able to facilitate N_2 reduction to a number of oxidation states, including S = 1 N_2^{2-}. Notably, this radical form is able to engage in extremely strong exchange coupling with paramagnetic metal ions.[11] We have therefore begun targeting the synthesis of complexes in which cyanide connects two electron-rich, low-coordinate transition metal fragments that are capable of significant π donation. The strong π-backbonding abilities of the three-coordinate molybdenum(III) complex $Mo(N^tBuAr)_3$ (Ar = 3,5-$Me_2C_6H_3$),[12] which facilitates both N_2 cleavage[13] and CN^- activation,[9] make this complex an appropriate metal fragment for this task. In this work, we report that a new high-spin iron(II) monocyanide building unit reacts with $Mo(N^tBuAr)_3$ to give a bimetallic complex in which cyanide bridges coordinatively unsaturated iron and molybdenum fragments. Structural and spectroscopic methods demonstrate significant activation of the bridging cyanide ligand in the bimetallic complex, and this activation gives rise to exceptionally strong antiferromagnetic coupling between the two metal ions.

The tris(carbene)borate iron(II) fluoride complex $PhB(^tBuIm)_3FeF$ (**1**) readily and cleanly reacts with equimolar Me_3SiCN to provide the corresponding terminal cyanide complex $PhB(^tBuIm)_3Fe(CN)$ (**2**) in high yield (Figure 1).[14] The solid-state structure of **2**, as determined by single crystal X-ray diffraction, confirms the presence of a single terminal cyanide ligand bound to a four-coordinate iron center. To the best of our knowledge, this four-coordinate geometry is unique for mononuclear iron cyanide complexes.[15] The Fe−C_{CN} distance of 2.058(4) Å is remarkably long for a metal−cyanide complex,[16] which is likely a consequence of the unusual high-spin, S = 2 ground state (see below). In contrast, the C−N bond length of 1.140(6) Å and Fe−C−N bond angle of 177.0(4)° are unremarkable, and the IR spectrum obtained for a solution of **2** (ν_{CN} = 2056 cm^{-1}) is consistent with a terminal cyanide ligand.[1] The bond distances between iron and the

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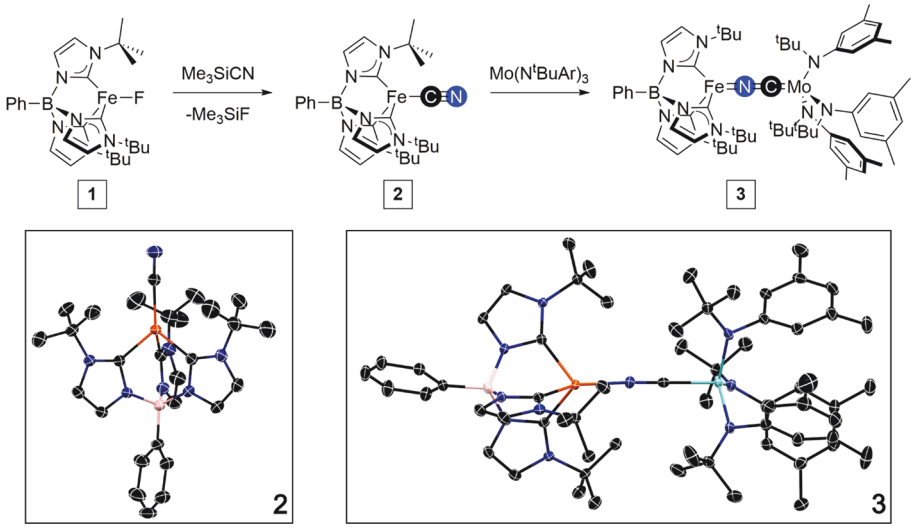

Figure 1. Upper: Synthesis of complexes **1**–**3**. Lower: Crystal structures of **2** and **3**, as determined by single crystal X-ray diffraction. Thermal ellipsoids are shown at 50% probability. Teal, orange, blue, black, and pink ellipsoids represent Mo, Fe, N, C, and B atoms, respectively; H atoms are omitted for clarity.

tris(carbene)borate ligand of 2.070(4)–2.101(3) Å are consistent with the high-spin iron(II) formulation.[17] The oxidation state and spin state of Fe in **2** are further corroborated by Mössbauer spectroscopy. At 80 K, the spectrum for a solid-state sample of **2** exhibits a symmetric quadrupole doublet (Figure S14), with a fit of the data providing an isomer shift of δ = 0.527(2) mm s^{-1} and a quadrupole splitting of ΔE_Q = 1.335(3) mm s^{-1}, in accord with other high-spin iron(II) tris(carbene)borate complexes.[17a,18] Taken together, these data establish **2** as a rare example of a high-spin iron(II) cyanide complex.[19,20]

As an initial demonstration of its utility as a building unit, **2** reacts with Mo(N^{t}BuAr)$_3$ to yield the cyano-bridged bimetallic complex PhB(^{t}BuIm)$_3$Fe(NC)Mo(N^{t}BuAr)$_3$ (**3**) (Figure 1). Inspection of the X-ray structure of **3** suggests that the cyanide ligand undergoes a linkage isomerism during the course of the reaction to give a Fe–N–C–Mo configuration. The relatively short Fe–N distance of 1.943(2) Å compares favorably with those observed in PhB(MesIm)$_3$Fe–NR$_2$ complexes[21] but is significantly longer than that observed in the Fe(I) complex, PhB(AdIm)$_3$Fe–N$_2$.[22] This suggests an Fe(II) oxidation state, which is supported by the spectroscopic, magnetic, and computational analysis (see below). The short Mo–C distance of 1.960(2) Å is slightly longer than that observed in ^{t}BuN≡C≡Mo(N^{t}BuAr)$_3$.[23] In addition, the C–N distance of 1.195(3) Å represents a slight elongation relative to that of 1.177(4) Å for uncoordinated cyanide.[24] These observations suggest that the cyanide ligand in **3** is activated with a formal bond order of less than three. This activation is more clearly observed in the cyanide stretching frequency, which is observed at an unusually low energy of ν_{CN} = 1793 cm^{-1} in the IR spectrum for **3** collected in THF (Figure S8). This low frequency is to be contrasted with the typical stretching frequencies of ca. 2000–2100 cm^{-1} observed for bridging cyanides.[1]

Spectroscopic methods were employed to provide further insight into the oxidation states of the two metal ions in **3**. The Mössbauer spectrum collected for a solid-state sample of **3** at 80 K (Figure 2) exhibits an asymmetric doublet with an isomer shift of δ = 0.663(2) mm s^{-1} and a quadrupole splitting of ΔE_Q = 1.476(2) mm s^{-1}. The isomer shift and quadrupole splitting are both consistent with a high-spin iron(II) formulation. The asymmetry of the quadrupole doublet for **3** likely arises from slow magnetic relaxation at low temperatures, as is often observed for mononuclear iron complexes.[25] This hypothesis is supported by the observation of a more symmetric doublet in the spectrum collected at 200 K (Figure S15). In addition, the Fe 2p X-ray photoelectron spectrum (XPS) for **3** is also consistent with high-spin iron(II), giving binding energies for the Fe 2p$_{3/2}$ line (709.62 eV) and shakeup satellite (714.05 eV) similar to those observed for other iron(II) tris(carbene)-borate complexes (Figure S16).[26] While the binding energy in the Mo 3d XPS (231.62 eV) suggests that molybdenum is in a higher oxidation state than +3 (Figure S17), a definitive assignment is difficult, likely due to the highly covalent bonding in the complex.[27]

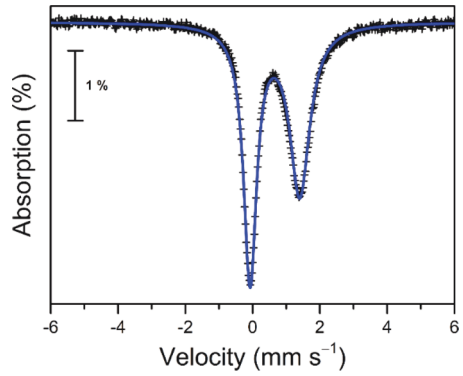

Figure 2. Zero-field ^{57}Fe Mössbauer spectrum for **3**, collected at 80 K. Black crosses correspond to experimental data, and the blue line corresponds to a fit of the data.

The collective structural and spectroscopic data for **3** suggest that strong π-backbonding from the highly reducing molybdenum tris(anilido) fragment leads to reduction of the bridging cyanide, with significant delocalization of unpaired electron density onto the ligand. The reduction of the C–N bond order in cyanide is rare and has previously only been proposed for the [Co(CN)$_3$]$^{6-}$ anion, where the cyanide

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stretching frequencies are in a range (ν_{CN} = 1600−1700 cm^{-1}) that suggests a $CN^{1.67-}$ formulation.[28,29] While not explicitly stated, the IR spectral data for the homobimetallic complex $(Ar^tBuN)_3Mo{\equiv}N{\equiv}C{\equiv}Mo(N^tBuAr)_3$ (ν_{CN} = 1575 cm^{-1}) is also consistent with reduction of the cyanide bond order. Finally, some chemical transformations have been proposed to occur via the intermediacy of a reduced cyanide ligand.[30,31]

We observe no spectroscopic evidence for dissociation of the bimetallic structure of **3**, as ascertained by variable-concentration ^{1}H NMR spectroscopy and supported by cyclic voltammetry (Figures S10 and S11). This finding is in contrast to many other cyanide clusters, which undergo dissociation or solvolysis reactions in solution. The high solution stability of **3** may provide evidence for the strong bonding interactions, and thus robustness, of the Mo−CN−Fe linkage resulting from strong π-backbonding.

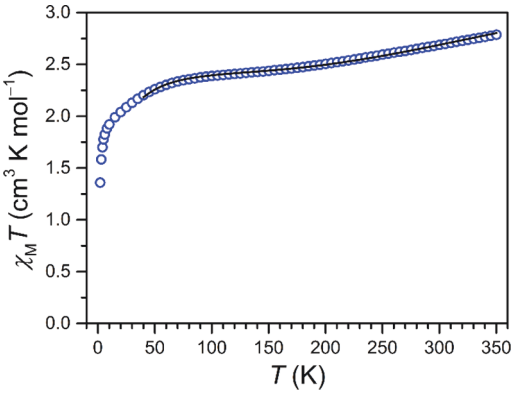

Figure 3. Variable-temperature dc magnetic susceptibility data for **3**, collected under an applied field of 1 T. Blue circles correspond to experimental data, and the black line corresponds to a fit of the data.

Variable-temperature direct current (dc) magnetic susceptibility data were collected for a solid-state sample of **3** under an applied field of 1 T (Figure 3). At 350 K, $\chi_M T$ = 2.79 cm^3 K mol^{-1}, much lower than the value expected for magnetically isolated S = 2 iron(II) and S = 1/2 molybdenum(III) centers. With decreasing temperature, $\chi_M T$ undergoes a gradual decline, reaching a plateau at ca. 160 K of 2.4 cm^3 K mol^{-1}, consistent with strong antiferromagnetic coupling between the spin centers to give an $S = {}^3/_2$ ground state. As the temperature is further decreased, $\chi_M T$ drops sharply to a value of 1.36 cm^3 K mol^{-1} at 2.0 K, likely the result of Zeeman splitting, magnetic anisotropy, and potentially weak intermolecular interactions. To estimate this antiferromagnetic exchange interaction, the data were fit in the temperature range of 40−350 K to a spin-only Hamiltonian, giving an exchange constant of J = −122(2) cm^{-1}, with g = 2.3(1) and D = −22(2) cm^{-1}.[32] To our knowledge, this value of J corresponds to the strongest magnetic coupling yet observed through a cyanide bridge, slightly eclipsing the previous record of J = −114 cm^{-1} observed for a V_3Mo_2 cluster.[8c]

Low-temperature magnetization measurements for **3** show a saturation of isofield curves well below the expected M = 3 μ_B for $S = {}^3/_2$, demonstrating the presence of strong magnetic anisotropy (Figure S22). Accordingly, variable-frequency alternating current (ac) magnetic susceptibility data reveal slow magnetic relaxation upon application of a 1200 Oe dc field (Figures S23−S25). A fit to the corresponding Arrhenius plot of relaxation time[33] gives a relaxation barrier of U_{eff} = 25(1) cm^{-1} with τ_0 = 3.4(4) × 10^{-6} s (Figure S26).

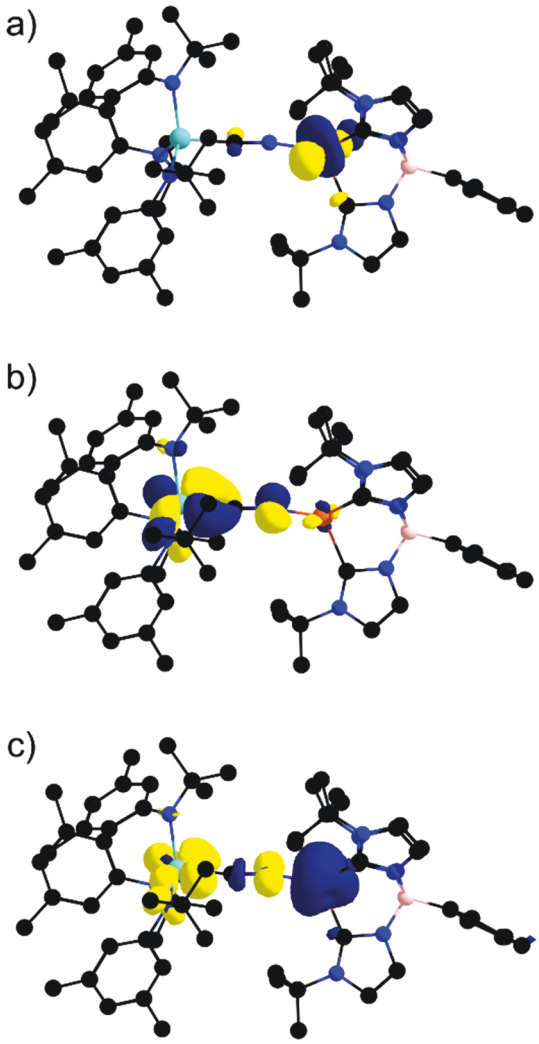

Figure 4. Magnetic pair of the (a) α and (b) β space for the $S = {}^3/_2$ broken symmetry surface, showing delocalization of β-spin density into the cyanide π^* orbital. Corresponding orbitals are shown at 0.05 isovalue; H atoms are omitted for clarity. (c) Spin density shown at a 0.005 isovalue with α-spin in blue and β-spin in yellow.

Density functional theory calculations were carried out to provide greater insight into the origin of the strong magnetic coupling in **3** (Figure 4). The magnetic orbitals, as determined by DFT methods (B3LYP-D3/def2-TZVP/def2-SVP), show that the α-spin density is primarily localized on iron, where the Mulliken spin density is 3.745 (Figure 4a). The β-spin density is localized on both molybdenum, where the Mulliken spin density is −0.580, and the N atom of the cyanide ligand, where it is −0.208 (Figure 4b). The overlap of the magnetic pair (Figure 4c) is consistent with strong antiferromagnetic coupling, and the calculated exchange coupling constant of J = −85 cm^{-1} (Yamaguchi formalism[34]) is in reasonable agreement with the experimental value.

The above results are in accord with a bonding model in which strong π-backbonding from molybdenum to the cyanide π^* orbitals delocalizes unpaired electron density onto the N atom of the cyanide ligand. In this model, the negligible β-spin density on the C atom (Mulliken spin density is −0.071) is a natural consequence of symmetry-allowed mixing with the

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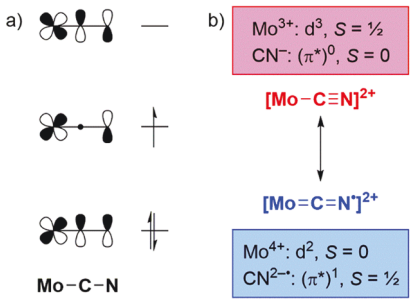

Figure 5. Bonding in the $\{MoCN\}^3$ fragment, illustrating how unpaired electron density is delocalized onto the N atom of cyanide. (a) Qualitative π-symmetry magnetic orbitals. (b) Resonance hybrid formulation.

cyanide π orbitals (Figure 5a).[35] This mechanism of delocalizing spin density onto the cyanide N atom leads to a stronger antiferromagnetic interaction with the unpaired electrons on iron. This bonding can also be considered using the Enemark−Feltham notation commonly employed to describe the highly covalent bonding of metal nitrosyl complexes.[36] Here, the $\{MoCN\}^3$ fragment[37] is considered as a single unit and can best be viewed as a resonance hybrid of the two limiting structures $[Mo^{III}-C\equiv N]^{2+} \leftrightarrow [Mo^{IV}=C=N\cdot]^{2+}$ (Figure 5b), giving a formal C−N bond order intermediate between 2.5 and 3.

This work demonstrates that the combination of strong π-backbonding and low-coordinate metal fragments can serve to significantly delocalize unpaired spin density onto a bridging cyanide ligand through reductive activation, resulting in unprecedented strong magnetic exchange coupling. We expect that this result exemplifies a general strategy for the synthesis of cyano-bridged clusters, and potentially solids, with unusually strong magnetic exchange coupling. Efforts are underway to employ **2** and related complexes as building units in the construction of novel metal−cyanide compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b09445.

Full experimental and characterization details (PDF)
Crystal structure data for complexes **1**−**3** (CIF)

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Notes

The authors declare no competing financial interest.

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