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 CoI3 cluster, Co3LEt/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 (μ3-η1:η2:η1-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.

Despite 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 metal−metal 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 CoBr3LEt/Me (1) to yield a metal−metal bonded 48-electron tricobalt(I) cluster, Co3LEt/Me (2). Reaction of 2 with N2 affords the dinitrogen-bridged complex Co3(N2)LEt/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 KC8 to a THF solution of reddish-purple 1 under an Ar atmosphere affords Co3LEt/Me, 2, in 32% isolated yield (Scheme 1, bottom).13 H NMR spectra of 2

Scheme 1. N2 Activation by Metal−Metal Bonded Complexes

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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 $\text{Ar}-\text{CH}_2$ and $\text{N}-\text{CH}_2$ protons (Figure S1).\textsuperscript{13} In the solid-state structure of 2, the [Co$_3$] core is ligated only by the cyclophane with each cobalt center in a distorted octahedral environment (Figure 1), comprised of the NAcNAC chelate ($\angle \text{NL}-\text{Co}-\text{NL} = 91.0-93.0^\circ$), two Co−Co interactions, and two $\eta^2$ interactions to the arenes (Figure 1B). The asymmetric $\eta^2$ 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.\textsuperscript{14} The Co$^+$ centers in 2 significantly $\pi$-backbond to the arene $\pi$ systems based on the slightly puckered arene rings and the upfield shifts of the $^{13}\text{C}$ NMR resonances for the arene $\text{C}$ atoms in 2 vs the free ligand (Figure S2).

The ligand cavity in Co$_3$L$_{Et/Me}$(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.\textsuperscript{11,25} 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.\textsuperscript{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).\textsuperscript{24} Thus, a better descriptor is an $\eta^1$-coordination mode to each Co center rather than an asymmetric $\eta^1$ 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.\textsuperscript{11,25}

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$_3$Br$_3$L$_{Et/Me}$ is a precatalyst for catalytic silylation of dinitrogen as reported previously, we saturated a room temperature solution of 2 with $\text{N}_2$ over 36 h to yield a new paramagnetic species, Co$_3$N$_2$L$_{Et/Me}$(3), which has $D_3h$ symmetry in solution based on $^1\text{H}$ NMR data (Figure S4).\textsuperscript{26} Complete conversion can be afforded at 70 °C after 1 h. Isotopically sensitive IR absorptions assigned as the $\text{N}_2$ stretching vibrations in Co$_3$N$_2$L$_{Et/Me}$ are observed at
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 \( N_2-Co-N_2 \) angles of \( \sim 100^\circ \) (Table S3). The Co–Co separations in 3 support cleavage of all metal–metal bonds upon encapsulation of a \( \mu_3-N_2 \) \( \eta^1 \) \( \eta^3 \)-dinitrogen within the internal cavity (Figure 1C). Positional disorder with respect to a minor impurity (modeled as <1%) and for the bound \( N_2 \) 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).\textsuperscript{27–29} IR spectra of a degassed toluene solution of \( \text{[Co}_{3}N_2] \text{Li}^{+} \text{Me}^- \) 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 \( N_2 \) 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 Co-ligand covalency with the frontier molecular orbitals exhibiting appreciable delocalization into the diketiminate chelates and backbonding between the Co ions and the \( N_2 \) ligand (Figure 2). The latter contrasts with the isosctructural \( \text{Cu}_{3} \) congener in which only metal–dinitrogen dispersive interactions are observed.\textsuperscript{30} The apparent ground state of the compound is a triplet resulting from moderate antiferromagnetic coupling (\( J = -132.78 \text{ cm}^{-1} \)) between the two cobalt centers that coordinate the \( N_2 \) ligand in an \( \eta^1 \) fashion. The calculated \( N_2 \) 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 \( N_2 \) ligand possesses double-bond character, as the calculated Laplacian of the electron density (\( \nabla^2 \rho \)) at the \( N-N \) bond critical point of \(-1.4228 \text{ au} \) is similar to that for \( N_2H_2 \) (\( \nabla^2 \rho = -1.4642 \text{ au} \)) and significantly higher than that for \( N_2 \) (\( \nabla^2 \rho = -2.9764 \text{ au} \)).\textsuperscript{29}

Of relevance here are the formally diiron(I) and dicobalt(I) compounds \( \text{L}^+\text{MNML}^+ \) (\( \text{L} = \text{HC}(\text{C}(\text{CH}_3)\text{N}(2,6- \text{ipr}_2\text{C}_6\text{H}_3))_2^{-} \) and the aforementioned \( \text{[(PNP)Co}_2 \text{N}_2] \).\textsuperscript{10,30,31} The \( \eta^2 \text{N}(N) \) in 3 compensates for the weaker \( \pi \) back-bonding interactions expected for cobalt(I) vs iron(I) (Table S2). Considering only the \( \mu_3-\eta^1:\eta^1 \) fragment of 3, the \( M-N \text{NN}=M-M \) unit is bent (\( \angle M-N=N-M = 129.0(14)^\circ, 134.5(15)^\circ \)) and more acute than those reported by Tomson and Mindiola and Caulton (\( \angle M-N=N-M = 155.1^\circ–163.2^\circ \)).\textsuperscript{32,33} Bonding of the \( M-N \text{NN}=M-M \) fragment is expected to diminish the metal–dinitrogen \( \pi \) overlap compared to the more linear mode. For example, \( \nu_{N=N} \) for \( \text{LFeNNFeL}^- \) is \( \sim 200 \text{ cm}^{-1} \) lower in energy than that for Tomson’s, and that for \( \text{K}_{2} \text{LFeNNFeL}^- \) in which two K⁺ cations are associated in a side-on fashion with the \( N_2 \) 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 \( \mu_3-\eta^1:\eta^1 \text{N}_2 \) vs \( \mu_3-\eta^1 \text{N}_2 \) compounds support this assertion as does the calculated 22 kcal/mol stabilization afforded by adding a third Fe center bound \( \eta^1 \text{N}(N_2) \) to the linear LFeNNFeL^- noted above.\textsuperscript{34,35}

A close analysis then of the occupied frontier MOs reveal a covalent \( \text{Co}–\eta^2 \text{N}(N) \) interaction with significant \( \pi^* \) character. To quantify the effect of this Co center, we modeled a complex in which a Co-diketiminate fragment was removed from 3 to afford a \( \mu_3-\text{dinitrogen} \) dicobalt species 4. The two remaining Co-centers in 4 coordinate the \( N_2 \) ligand in an \( \eta^1 \) fashion similar to that found in 3, rather than isomerizing to a \( \mu_3-\eta^1:\eta^1 \) 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 \( \nu_{N=N} \) 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 \( N_2 \) 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–\( N_2 \) 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.\textsuperscript{36} Given this precedent and that 1 effects \( N_2 \) reduction to \( \text{N}(\text{SiMe}_3)_2 \),\textsuperscript{26} \( \text{Co}_2\text{N}_2\text{L}^{3+}/\text{M}^+ \) was reduced with \( \text{KC}_8 \) and a silyl electrophile under an Ar atmosphere, yielding 0.6 equiv of \( \text{N}(\text{Me},\text{Si})_3 \) after analysis of the acid-quenched filtrate by \( ^1H \) NMR spectroscopy (Figure S7). The \( N_2 \) donor in 3 is, therefore, primed for further activation and bond scission, supporting 2 and 3 as possible intermediates in the catalytic silylation of \( N_2 \) 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.\textsuperscript{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. \( \text{Co}_2\text{N}_2\text{L}^{3+}/\text{M}^+ \) features a \( \mu_3-\eta^1:\eta^1 \text{N}(N) \) coordination mode for dinitrogen, drawing parallels to the bent coordination in this and related systems are underway, as well as the potential of the \( \text{[Co}_3 \) 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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