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Insights into small molecule activation by multinuclear first-row transition metal cyclophanates

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The rational design of trimetallic transition metal clusters supported by a trinucleating cyclophane ligand, $\mathbf{L}^{3-}$, and the reactivities of these complexes with dinitrogen and carbon dioxide are discussed. Emphasis is placed on the differences in the observed reactivity between these trimetallic cyclophane complexes and that of the mono- and dinuclear transition metal compounds.

Introduction

Bioavailable nitrogen (*e.g.*, ammonia) is crucial to life on earth as N atoms are principal building blocks of proteins and nucleic acids.[1] Although the planet's atmosphere is predominantly composed of N_2 gas (78%),[2] the strong triple bond between the two N-atoms renders N_2 as chemically-inert. However, the conversion of dinitrogen to ammonia is thermodynamically favourable ($\Delta H^\circ = -92.22$ kJ mol^{-1}; $\Delta G^\circ = -16.48$ kJ mol^{-1}) albeit kinetically limited under ambient conditions.[3] Currently, atmospheric dinitrogen is converted to ammonia in two principle systems: N_2 fixation by the nitrogenase family of enzymes in *Rhizobacter*,[1,4] and industrially using the Mittasch catalyst in the Haber–Bosch process (HBP).[5] The HBP requires high temperature and pressure of N_2 and H_2, which in part accounts for the large energy demands (~1% of global energy consumption) of this process.[5a,6] The HBP is exceptionally energy efficient on large scale production, but it unfortunately relies on fossil fuels (inc. dihydrogen derived from methane). Such centralized production inherently incurs distribution costs, which can be prohibitively expensive depending on the end user's location (*e.g.*, sub-Saharan Africa). Discovering alternative strategies for decentralized N_2 fixation are thus critical given the importance of ammonia as an N source for crop plants and as a synthon for commodity chemical production. These approaches can operate at lower efficiencies provided that they utilize renewable energy sources (*e.g.*, solar) to drive the chemistry.

The biological method for N_2 fixation is indeed decentralized with "local" and on-demand NH_3 production afforded by the symbiotic relationship between the host plant and the bacteria. This process is energetically inefficient, consuming 16 equivalents of ATP per N_2 molecule,[1] and it is difficult to extend this approach to a broad range of crop plants; transposing the genes or recreating the symbiotic relationships remain unrealized.[7] The nitrogenase enzymes utilize a polynuclear iron sulfur cluster of the type Fe_7S_9MC, where M = Mo, Fe, or V, as the active site for N_2 reduction (Fig. 1).[8] These enzymes operate under ambient temperature and pressure, suggesting that similar small scale low temperature synthetic systems can be viable alternatives to the HBP. Inspired in part by the multimetallic nature of the nitrogenase cofactors and more broadly by the plethora of multimetallic cofactors that activate small molecule substrates (*e.g.*, Cu_Z in nitrous oxide reductase and $NiFe_4S_s$ cluster in NiFe carbon monoxide dehydrogenase),[9] we

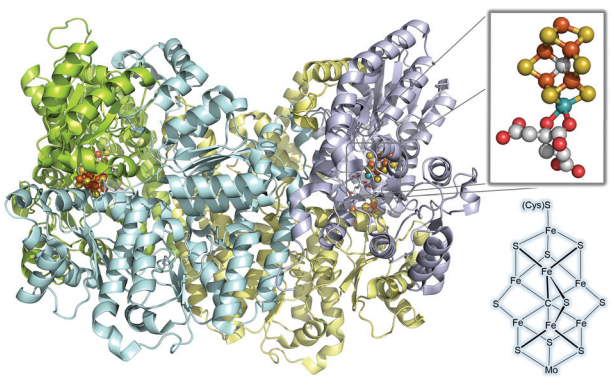

Fig. 1 Crystal structure of the MoFe protein (left), the iron-molybdenum cofactor or FeMo-co (top right), and a schematic representation of the cofactor (bottom right). The α, β, γ, and δ subunits are represented ribbon diagrams in green, teal, purple, and yellow, with the metal cofactors depicted as spheres. Carbon, oxygen, sulfur, iron, and molybdenum atoms are shown in grey, red, yellow, orange, and teal spheres. Crystallographic coordinates obtained from PDB entry 3U7Q.

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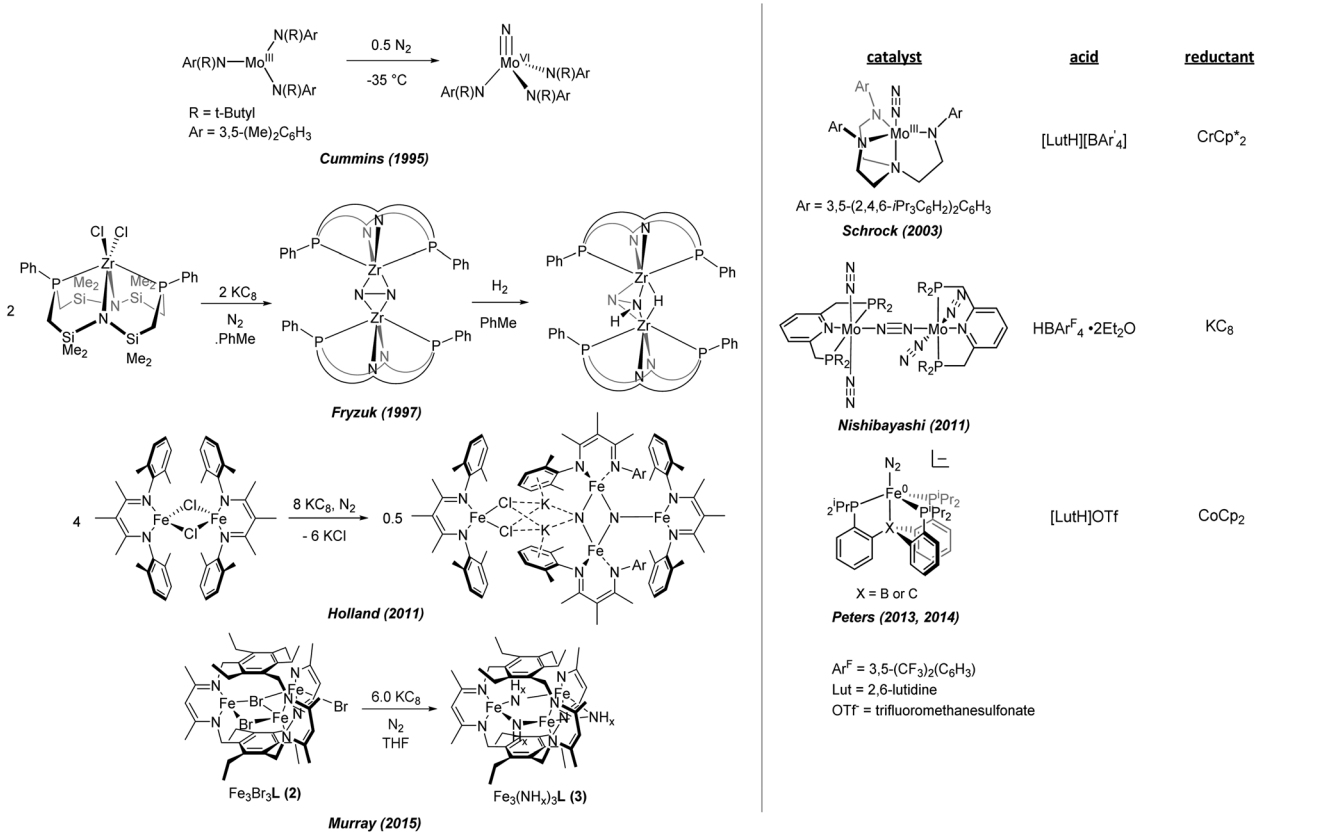


Scheme 1 Selected stoichiometric and catalytic systems for N_2 activation.

and others[10] have targeted multimetallic complexes as possible reaction sites for the dinitrogen activation and fixation.

Since Senoff and Allen reported the first N_2-bound transition metal complex, a large number of dinitrogen complexes and systems that activate N_2 by partial or complete scission of the N≡N bond have been reported.[11] Cummins and Laplaza described the rapid cleavage of atmospheric dinitrogen by a three-coordinate molybdenum(III) complex at −35 °C to form two terminally-bound Mo(VI) nitrides (Scheme 1).[12] Shortly thereafter, Fryzuk and coworkers reported a Zr(IV) system that cleaves the N≡N triple bond of dinitrogen to form a dizirconium-hydrazide which generates a $Zr_2(\mu{:}\eta^2\text{-}N_2H)(\mu\text{-}H)$ imido complex.[13] The Schrock group was the first to report catalytic reduction of N_2 to NH_3 by a discrete monometallic complex using stepwise addition of a reductant and proton source.[14] Nishibayashi and coworkers demonstrated that a PNP-pincer supported Mo(III) chloride binds N_2 upon reduction and catalytically generates NH_3 in the presence of a mild reductant and acid.[15] Iron systems competent for N_2 cleavage have similarly been reported. Tyler demonstrated that a low-spin monoiron complex that binds atmospheric dinitrogen would subsequently liberate ammonia and hydrazine upon addition of a strong acid.[16] More recently, Rodriguez *et al.* communicated that reduction of a (β-diketiminato)iron(II) dimer under an N_2 atmosphere affords a self-assembled tetrairon di(nitride) complex.[17] The two nitride ligands can be released as ammonia by treating the cluster with a proton source. Finally, Peters and coworkers reported the first catalytic systems employing iron, in which a family of tripodal iron complexes allow for detailed examination of N_2-binding, formation of terminal nitrides, N–H bond formation, and NH_3 production.[18] In all of these cases, the focus is primarily on the design of monometallic complexes, despite evidence suggesting that multiple metals may be involved in N_2 scission.

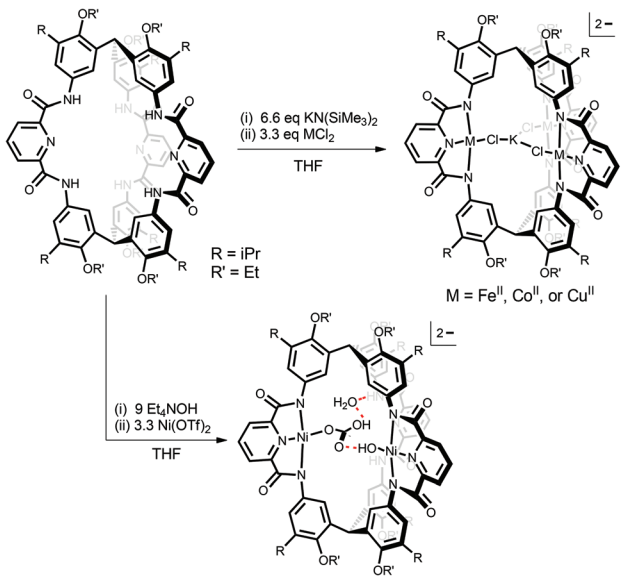
Macrobicycles as ligands for multimetallic compounds

In considering the design of multimetallic compounds, one can develop ligands that either promote or preclude direct metal–metal interactions. In the case of direct metal–metal interactions, Berry,[10j,k] Betley,[10f–h] Lu,[10a–c], and Thomas,[10d,e] among others have made important and exciting contributions and demonstrated profound and diverse reactivities. By inhibiting direct metal–metal interactions, however, the effect of metal ion proximity can be directly evaluated by comparing the reactivity of the monometallic complexes with that of the multimetallic congeners. In addition, this design approach simplistically treats the multimetallic complex as an aggregate of individual monometallic units in which the relative orientation of the frontier orbitals of each fragment and the distance between the metal ions can be controlled and varied. The ligand in this approach must enforce a narrow range of metal–metal distances to favour substrate binding,

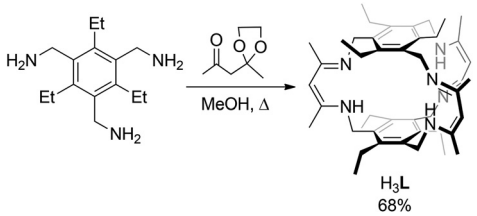
but prevent metal–metal bond formation. One family of organic compounds that meet these criteria are macrobicycles, which we[19] and others[20] have employed extensively as ligands for tri- and di-metallic complexes.

Our first generation macrobicyclic ligand utilized derivatized triphenylmethane fragments as caps and pyridine-2,6-dicarboxamide arms.[19a,b] Deprotonation of the six amides of this ligand followed by metalation afforded the corresponding trimetallic complexes with each metal held in the *N*,*N*,*N*-chelate of each arm (Scheme 2). The resultant complexes are predominantly anionic, however, with the fourth coordination site in the square plane occupied by a halide donor in all complexes except for the trinickel(II) species. Disappointingly, the accessible axial coordination sites of each metal in these complexes are not oriented towards the internal void space. Nonetheless, O-atom transfer (albeit ineffective) from iodosobenzene to triphenylphospine is possible using the tri(chloroiron(II)) complex. In reactions using substoichiometric equivalents of base and acetonitrile, we were also able to access complexes in which the metal ions are coordinated by an *O*,*N*,*O*-chelate rather than the *N*,*N*,*N* one. More interestingly, dimetallic complexes could be readily accessed by varying the base in the reaction, which lead to the discovery of CO_2 capture from ambient air by presumed terminal copper(II) and nickel(II) hydroxide species.

With these drawbacks in mind, the subsequent ligand design diverged from the triphenylmethane building block and instead utilized 1,3,5-tri(aminomethyl)-2,4,6-triethylbenzene. Anslyn and coworkers highlighted the preferential alternating up-down configuration as key for maximizing synthetic yields.[21] The ethyl groups should also allow for facile access of substrates to the central cavity. Indeed, the tris(pyridine-2,6-dicarboxamide) cyclophane of this cap functions as an organic receptor with rapid diffusion of acetate and other anions into the central cavity.[22] The β-diketiminate was selected as the donor arm because the extensive literature precedent on the reactivity of mononuclear (β-diketiminato)metal complexes can be contrasted to the that observed for metal complexes of this cyclophane (Scheme 3).[23] Similar metalation strategies afford the expected trimetallic complexes.[19c,d,k] The chemistry of these compounds will be the primary focus of this Perspective.



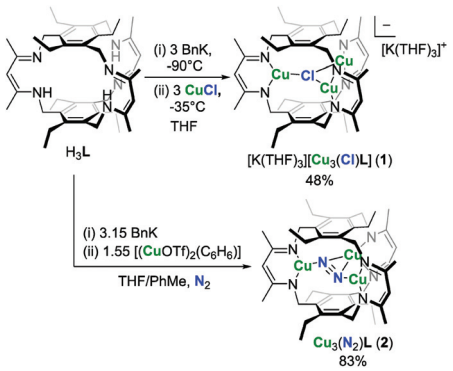
Scheme 2 Synthesis of di- and trimetallic compounds using a tris(pyridine-2,6-dicarboxamide) cryptand. Hydrogen bonds in the dinickel species are depicted as red dashed lines. Adapted from ref. 19*a* and *b*.



Scheme 3 Synthesis of tris(β-diketimine) cyclophane, H_3L. Adapted from ref. 19*c*.

N_2 binding and cleavage by trimetallic cyclophanates

The tricopper(I) cyclophanate complex was an early target because of our interest in modelling the active site of multicopper oxidases (MCOs) and other multicopper active sites in biological systems.[24] Addition of benzylpotassium to solutions of H_3**L** in THF generate the tripotassium salt (K_3**L**) which, upon metalation with cuprous chloride *in situ*, yielded the anionic complex $[Cu_3(\mu_3\text{-Cl})\mathbf{L}]^-$ (**1**) (Scheme 4).[19d] From the crystal structure, the copper–copper distances in **1** range from 4.1–5.0 Å and are comparable to those observed in the tricopper active site of MCOs.[25] Our initial attempts to probe the reactivity of this complex with dioxygen were challenging; the reaction kinetic traces were complex and not readily modelled. We sought to remove the internal chloride from the complex, as chloride dissociation could contribute to the observed complexity. Using a similar metalation strategy but with a larger counter anion for the copper(I) source (*i.e.*, CuBr or



Scheme 4 Synthesis of tricopper(I) clusters $[K(THF)_3][Cu_3(Cl)L]$ (**1**) and $Cu_3(N_2)L$ (**2**). Adapted from ref. 19*d* and *e*, respectively.

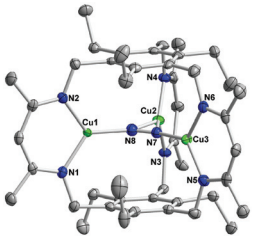


Fig. 2 Crystal structure of $Cu_3(N_2)$**L** (**2**) at 60% thermal ellipsoids. C, N, and Cu atoms depicted as gray, blue, and green ellipsoids. H-atoms and solvent molecules are omitted for clarity. Adapted from ref. 19*e*.

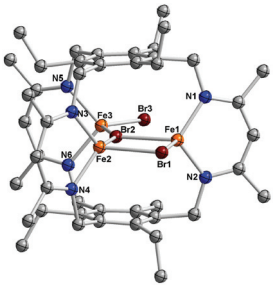
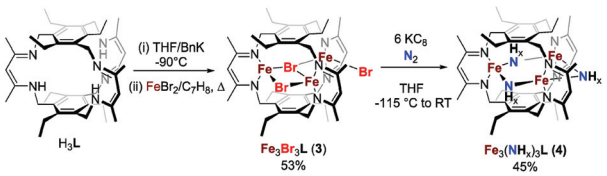


Fig. 3 Crystal structure of Fe_3Br_3**L** (**3**) at 90% thermal ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity. C, N, Fe, and Br atoms depicted as gray, blue, orange, and maroon ellipsoids, respectively. Adapted from ref. 19*c*.

$[Cu(OTf)]_2(C_6H_6)$), we were surprised to isolate a (μ–η^1:η^2:η^1-dinitrogen)tricopper(I) complex, **2** (Fig. 2).[19e] This compound represents the first molecular complex containing Cu–N_2; previously, Cu(I)–N_2 species have been observed in the gas phase or in copper(I)-doped porous solids.[26] The N≡N bond distances in **2** (1.0956(1)–1.0854(1) Å) are shorter than in free N_2, which seem to contradict the N–N stretching mode at 1952 cm^{-1} – almost 400 cm^{-1} lower in energy than that for free N_2 – observed in resonance Raman spectra collected on $Cu_3(N_2)$**L**. In addition, DFT calculations on optimized structures of **2**, in which a methyl-for-ethyl substitution was employed for the arene caps, are consistent with minimal π-backbonding as evidenced by the computed N–N bond distance (1.125 Å) and the N–N vibrational frequency (2094 cm^{-1}). Given these conflicting results, we noticed in DFT calculations that decreasing the size of the alkyl substituents on the ligand resulted in greater N–N activation. We, therefore, suggested that the N–N distance in the solid state may be influenced by crystal packing effects that force the complex to adopt a conformer with a lesser degree of N_2 activation whereas the vibrational data reflect the greater flexibility in the solution state that allows the compound to sample conformers with a more activated N_2 ligand. Fortuitously, the coordination mode of dinitrogen in the $Cu_3(N_2)$**L** complex bears strong resemblance to the computational model proposed by Cundari and Holland, in which the side-on coordination of a third iron(I) center was required for N–N bond scission. This tricopper(I)–dinitrogen complex can be thought of as a potential intermediate analog along the dinitrogen activation pathway by low valent (β-diketiminato)metal complexes.[17,27]

Part of the inspiration for the cyclophane design stemmed from Holland's work on N_2 activation, and in particular, their report of dinitrogen activation upon reduction of a (β-diketiminato)iron(II) chloride complex.[17,28] There, the N_2 derived fragment is best described as three iron centers bridged by two nitride donors; thus, our ligand seemed to provide a direct route to probing if three iron atoms are competent for N_2 bond scission. The triiron(II) tri(bromide) complex, Fe_3Br_3**L** (**3**), could be readily accessed using our general protocol.[19c] Each Fe(II) center in this compound is pseudo-tetrahedral, supported by the *N*,*N*-chelate of a β-diketiminate arm and two bromide ions (Fig. 3). Initially, three equivalents of potassium graphite were used to investigate N_2 activation by **3**; we anticipated formally reducing each iron center to the monovalent state followed by a six electron reduction of N_2 to generate a triiron(III) di(μ-nitride) species. Surprisingly, the triiron complex, $Fe_3(NH_x)_3$**L** (**4**), was instead the observed product (Scheme 5). Subsequently, the reaction conditions were optimized to maximize the yield of NH_3 released from acid hydrolysis of the product, which corresponded to 6 equiv. of KC_8. Curiously, dinitrogen reduction appears to funnel into the $Fe_3(NH_x)_3$**L** product and we remain unable to isolate complexes with fewer N_2 derived N-atoms by starving the reaction of reducing equivalents. The degree of protonation of the N_2 derived ligands is likely a mixture of amide and imide donors, leading to mixed valent compounds as determined from our Mössbauer spectra. The designed approach employed by us evidently leads to reactivity differences from the monometallic systems, strongly suggesting that we access distinct cooperative pathways as compared to the self-assembled monometallic system. The interplay between the limited conformations and the enforced orbital interactions in our complexes as compared to those for the monometallic system are undoubtedly important.

The notable differences in our result as compared to previous work are that all N-atom bridges are protonated, and that we incorporate *three* N-atoms.[19f] The proton source remains undetermined in this reaction, but we can exclude adventitious water on the glass surface and solvent protons. This was possible by evaluating the reduction products for reactions performed in silylated glassware and in deuterated solvents, respectively. Therefore, the ligand C–H bonds remain likely candidates of these protons. Protonation of transient nitrides as in our system likely tunes the reduction potential of



Scheme 5 Synthesis and reduction of Fe_3Br_3**L** (**3**). Adapted from ref. 19*f*.

the cluster, opening access to further reductive chemistry. Evidence in support of this hypothesis has recently been provided by Holland and coworkers as well as the surprisingly low one-electron redox process observed for $Fe_3(NH_2)_3$**L** (~−0.85 V *vs.* Fc/Fc^+).[38,19h]

The presence of a third N-donor implicates at least one intercluster step occurs during reduction of dinitrogen. Although the approach of two triiron complexes seems unlikely from a steric perspective, we were fortunate to obtain the solid-state structural solution of a dimeric product (**5**), which co-crystallized with **4** from a reaction (Fig. 4).[19f] The interdigitation of the ethyl substituents on the caps and the methyl groups on the diketiminate arms affords a suitable binding site for two K^+ cation at the interface. The structure bears strong similarities to the K^+ incorporation in other di-, tri-, and tetrairon compounds containing a bridging N_2 or two N^{3-} donors.[17,28]

Evidence for an intercluster pathway brings in to question whether metal–metal interactions within a cyclophanate complex are important for N_2 activation or if N_2 undergoes bond cleavage only at the interface between two complexes (Scheme 6). The dibromo(μ_3-nitrido)triiron complex **7** could be an intermediate along an intercluster-only mechanism with

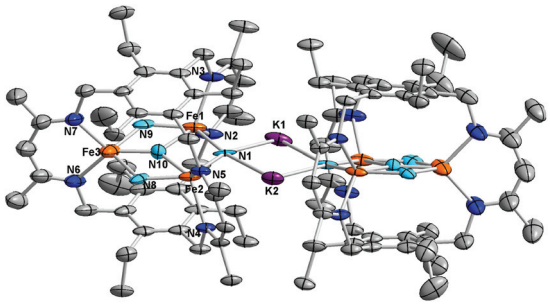
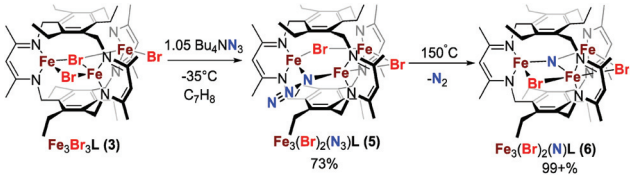


Fig. 4 Solid-State structural solution of **5** at 50% thermal ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity. C, N, Fe, and K atoms depicted as gray, blue, orange, and purple ellipsoids, respectively. Bridging atoms modelled as nitrides are shown as light blue ellipsoids. Adapted from ref. 19*f*.

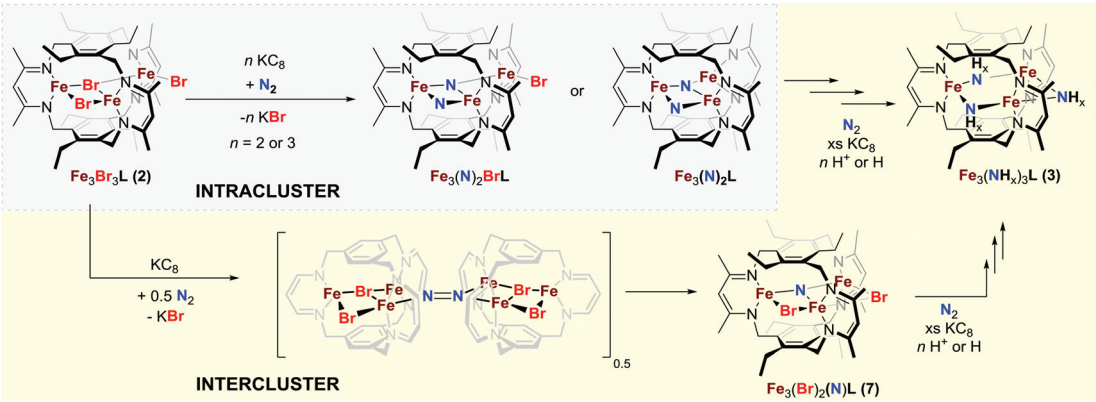


Scheme 7 Synthesis of $Fe_3(Br)_2(N)$**L** (**7**). Adapted from ref. 19*h*.

the reactivity of this species providing support for either pathway. $Fe_3(Br)_2(N_3)$**L** (**5**) was prepared by substitution of one halide in **3** with azide (Scheme 7). Thermolysis of **5** in the solid state resulted in the loss of azide vibration (2082 cm^{-1}) by IR spectroscopy and the isolation of **6** as an olive green solid. As for Fe_3Br_3**L**, there are no reversible redox couples observed in cyclic voltammograms of **6** up to −2.5 V *vs.* Fc/Fc^+. Moreover, preliminary attempts to reduce dinitrogen by treating **6** with a strong reductant have been unsuccessful, independent of the number of equivalents of KC_8 added. These data provide early support that the intracluster pathway is important for dinitrogen activation in our system. Admittedly, protons can tune the reactivity and electrochemical properties of these complexes and are not considered in attempts to reduce dinitrogen starting with **6**; that is, coupling proton and electron delivery may turn-on the reactivity of **6** or reduced variants towards N_2.

Substrate specific reactivity of hydride-bridged trimetallic complexes

The mechanism for dinitrogen reduction by FeMoco proposed by Hoffman, Seefeldt, and Dean relies on the reductive elimination of two iron hydrides to generate the reactive species that binds N_2.[1,4b,29] Relatedly, hydride complexes of various transition metals can readily eliminate H_2 and subsequently bind N_2.[30] In essence, these hydride ligands mask low valent metal centers, and protecting reducing equivalents prior to reaction with dinitrogen. Photochemical or thermal reductive elimination occur in the di(μ-hydrido)dimetallic complexes sup-

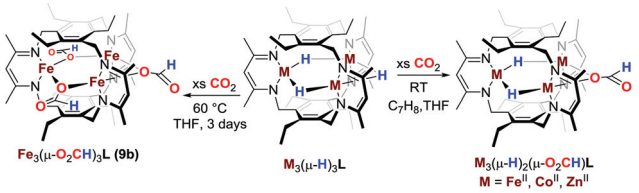


Scheme 6 Proposed inter- and intracluster pathways for dinitrogen cleavage upon chemical reduction of Fe_3Br_3**L** (**3**) in yellow and black backgrounds, respectively. Adapted from ref. 19*h*.

ported by β-diketiminates.[28,31] Hydride-decorated trinuclear transition metal clusters supported by our cyclophane were, therefore, a natural extension in our studies on dinitrogen activation. These metal hydride clusters could provide insight into the enzymatic reaction as well as the potential cooperative events on the iron face of the Mittasch catalyst during the Haber-Bosch process.

Reaction of M_3Br_3**L** (where M = Fe^{II} or Co^{II}) with potassium superhydride generates the corresponding trihydride complex, $M_3(\mu\text{-}H)_3$**L** (where M = Fe^{II} and Co^{II}).[19i] Neither thermal nor light-driven H_2 reductive elimination could be accessed in these systems, and no reactivity with N_2 was observed as expected. The inability to eliminate H_2 is likely because the hydride-hydride distances are considerably longer (2.7608(1)–3.3670(2) Å) than in the dimeric compounds, and prevent the necessary orbital overlap to form the H–H bond. The order of dinitrogen binding and dihydrogen loss from some metal hydrides, however, is uncertain.[32] For FeMoco, one can envision N_2 association instigating H_2 loss rather than H_2 elimination occurring prior to substrate binding.[29] We, therefore, began to survey a variety of substrates with the expectation that either hydride insertion or reductive elimination could be observed. To our surprise, IR and NMR spectra provided no evidence for reaction with benzonitrile, acetonitrile, benzaldehyde, acetone, or carbon disulphide. However, carbon dioxide cleanly reacts with both the triiron(II) and tricobalt(II) trihydrides over the course of several days at room temperature to afford the (μ-1,1-formato)di(μ-hydride)trimetallic complexes (Fig. 5). In the case of the triiron trihydride complex, all three hydrides can be forced to insert into CO_2 by using elevated temperatures to give the tri(μ-1,1-formate) complex, which was not observed for the cobalt congener (Scheme 8). This difference in reactivity between Co_3H_3**L** and Fe_3H_3**L** likely arises from the difference in the metal-hydride bond strengths.

The observed high specificity for CO_2 was unprecedented, and the muted reactivities of the three hydrides donors in these complexes are unusual. A steric component to the substrate specificity is likely as substrates must navigate the narrow space between the two ethyl substituents, although electronic effects are also certainly present as suggested by the



Scheme 8 Reactivity of trimetallic trihydrides with CO_2.

contrasting reactivities of the Co and Fe systems. In order to probe the steric effects and to more rapidly screen substrates, we targeted the trizinc congener and employed NMR spectroscopy to evaluate reaction mixtures.[19g] In addition, zinc hydrides typically exhibit broad substrate functional group scope for hydride transfer, and changes to that reactivity profile in our system would likely arise from steric effects.[33] Here again, we observed no reactivity over a 24 h period for the nitrile and carbonyl substrates or CS_2. Even more surprisingly, Zn_3H_3**L** is unreactive towards protic solvents over the same time course, and is air-stable as a solid; NMR spectra for samples with added methanol or water are unchanged. This tolerance to protic solvents – in particular, water – and ambient moisture were previously unprecedented for zinc hydrides. As for the iron and cobalt clusters, Zn_3H_3**L** reacts readily with CO_2 to generate the analogous formate-di(hydride) complex.

The causes of the high specificity for CO_2 by these compounds remain unclear. One could envision that the ligand exerts strong size discrimination on substrates as suggested from the space-filling models of these complexes. Rotation of the ethyl groups is thermally accessible at room temperature and in solution, based on work by Anslyn, which would serve to further limit substrate access.[21] Such an argument rationalizes the lack of reactivity towards the tested nitrile and carbonyl substrates, but seems unlikely for CS_2, H_2O, and CH_3OH. Computational studies suggest that the reorganization of CS_2 upon nucleophilic attack is higher than that for CO_2 and dictates the selectivity observed for frustrated Lewis pairs and could similarly apply to our system.[34] The electrostatic poten-

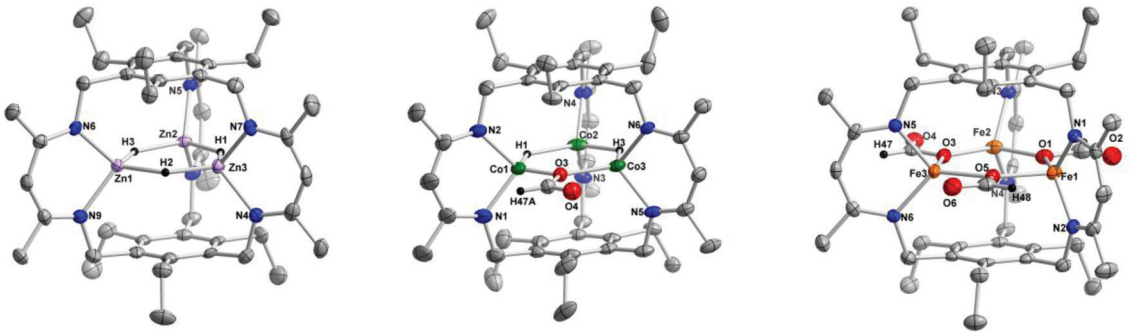


Fig. 5 Solid-State structure of Zn_3H_3**L** (left), $Co_3(\mu\text{-OCHO})(\mu\text{-H})_2$**L** (center), and $Fe_3(\mu\text{-OCHO})_3$**L** (right) at 80%, 50%, and 80% thermal ellipsoids, respectively. Hydrogen atoms and solvent omitted for clarity (except for hydride and formate protons). C, N, Fe, Co, Zn, and O atoms depicted as gray, blue, orange, green, lavender, and red ellipsoids, and H-atoms as black spheres. Adapted from ref. 19*g* and *i*.

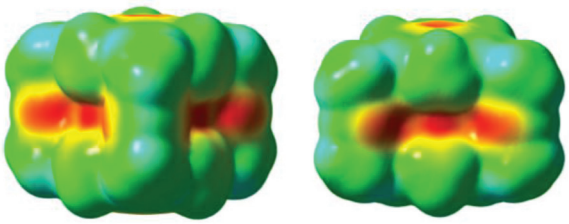


Fig. 6 Calculated electrostatic potential surface of a modified Zn_3H_3**L** in which ethyl groups are replaced with methyl ones. Adapted from ref. 19*g*.

tial surface of a modified Zn_3H_3**L** (*i.e.*, a methyl-for-ethyl substitution was used for computational ease) illustrates that each hydride donor is buried within a aliphatic groove (Fig. 6). The consequence of this may be that water is unreactive because approach of polar substrates to the hydride is retarded by the non-polar pocket, drawing parallels to selectivity based on substrate polarity in enzyme systems.[35] Previously, Holland and Schulz reported β-diketiminato-iron(II) and zinc(II) hydrides that crystallize as hydride-bridged dimers in the solid-state, which dissociate into the reactive monomers in solution.[31,36] A similar dissociative mechanism seems unlikely in our system given the structural constraints enforced by the macrobicyclic ligand. However, a fluxional bridging-to-terminal coordination mode of one or more hydrides could occur may explain the observed reactivity (*i.e.*, only one site reacts at room temperature) and slow rate of insertion into CO_2 as compared to the monometallic complexes. This proposed mechanism is consistent with the difference in reactivity of Co_3H_3**L** and Fe_3H_3**L** at elevated temperatures (*viz.* the tri-(formate) complex is only observed for the Fe variant). Fluxional behaviour, however, would suggest that conformations that are susceptible to reductive elimination might be accessible under the appropriate conditions. Indeed, we recently observed that Fe_3H_3**L** reacts with CO to eliminate H_2 and generate $[Fe(CO)]_2(FeH)L$, which is the first isolable complex containing low-valent iron centres in this ligand.[37]

Conclusions and outlook

Macrobicycles have been long overlooked as potential ligands for supporting complexes for small molecule activation, with the primary role of these organic cages as selective hosts for analyte recognition. Here, we highlight the diverse reactivities and structure types of trimetallic complexes supported by one cyclophane; these compounds stabilize Cu(I)–N_2 interactions at ambient temperatures and exhibit exceptional substrate specificity for hydride insertion into CO_2. As predicted, our initial studies indicate the reactivity profile of preassembled trinuclear clusters departs from that of monometallic congeners; for example, N_2 cleavage upon reduction of a triiron(II) cyclophanate results in protonation of N_2 derived ligands and incorporation of three N-atoms per complex. In addition, the ability to partially metallate these ligand types hints at facile routes to probing how secondary coordination effects, and hydrogen-bonding interactions in particular, tune the reactivity of multiple metal centres; for instance, the internal cavity and hydrogen bonding partners can orient substrates in a stereospecific manner for O-atom transfer. This distinct differentiation from the monometallic and self-assembled systems bodes well for future exploration of macrobicycles with other donor arms, and opens an almost limitless landscape for potential new reactivity from the controlled design of multimetallic compounds. In particular, the ability to readily tune the ligand sterics, such as substituting Me for Et on the benzene caps of our cyclophane, and varying the metal–metal distances, will allow us to probe the nature of selective reactivity with CO_2, the factors that influence potentially fluxional coordination of hydride donors, and the effect of metal ion type on reactivity.

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