Additive Effects in Metal-Lewis Acid Cooperativity Assessed in a Tetrahedral Copper-Hydrazine Complex Featuring an Appended Borane

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Supporting Information Placeholder

ABSTRACT: Within metal-ligand cooperative systems employing acidic groups, studies that empirically assess distance relationships are needed to maximize cooperative interactions with substrates. We report the formation of two Cu(I)-N_2H_4 complexes using 1,4,7-triazacyclononane (TACN) ligand frameworks bearing two *tert*-butyl groups and either a Lewis acidic trialkylborane or an inert alkyl group. Metal-Lewis acid cooperativity imparts heightened acidification of the hydrazine substrate and plays a key role in substrate release to a competitive Lewis acidic group.

The environment surrounding the active site(s) of metalloenzymes features flexible and dynamic amino acid networks to assist selective substrate binding and/or facilitate subsequent transformations.[1] Despite the prevalence of such secondary sphere interactions in biology, these design features are underexplored in the field of synthetic transition metal chemistry, where emphasis is often placed on primary sphere ligand tuning to effect substrate transformations.[2] To address this knowledge gap, a major thrust of our group's efforts,[3] and others,[4] is to examine requirements of tethered acidic groups in metal systems to facilitate substrate binding and reactivity. We previously described ideal-fit conditions (geometric and distance requirements) for cooperative binding modes of μ-1,1 and μ-1,2 substrates in tetrahedral complexes using bidentate and meridional tridentate ligand platforms.[3a,5] Importantly, such secondary-sphere design rules are dependent on how the appended groups are anchored to a given primary sphere ligand. Thus, because optimized parameters for substrate binding are ligand dependent, empirical studies are needed to clarify substrate binding requirements across different classes of primary sphere ligand environments.[6]

Recently, we described a facially-coordinating ligand, ^{BBN}TACN^{tBu}, containing an appended borane Lewis acid that is capable of stabilizing a monomeric copper hydride.[7] When treated with CO_2, a dimeric product formed where a formate unit acts as a bridging ligand between the Cu and appended boron of a second molecule (Fig. 1). This observed binding mode demonstrates that the coordination geometry required for a μ-1,3-substrate, such as formate to bind cooperatively at a single metal center, is mismatched for this system. To further clarify binding preferences, we aimed to expand on the known substrate reactivity at [(^{BBN}TACN^{tBu})Cu(I)] to determine requirements for mononuclear metal/Lewis acid cooperative binding.

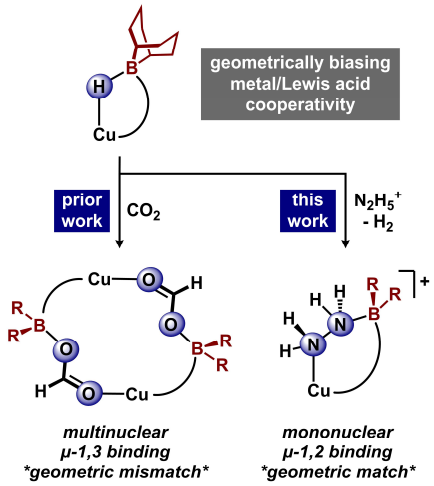
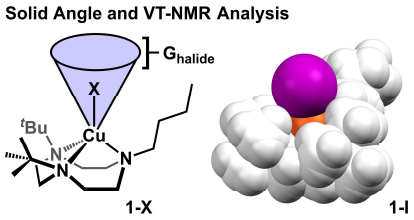


Figure 1. Prior work revealed geometric mismatches for μ-1,3 substrates. This work biases cooperative mononuclear μ-1,2 substrate binding.

To establish binding preferences, we sought to identify an ideal spectroscopic handle to use in the characterization of new (^{tBu}TACN^{tBu})Cu(I) complexes. We selected the ^{nBu}TACN^{tBu} ligand variant, which features an inert –CH_3 moiety in place of the trialkylborane, and targeted the synthesis of a series of halide complexes (Cl, Br, I). Treating a THF solution of ^{nBu}TACN^{tBu} with CuX at room temperature afforded (^{nBu}TACN^{tBu})CuX (**1-X**; X = Cl, Br, I) as white powders. The solid-state structures of **1-X** revealed tetrahedral geometry (τ_4 = 0.65) and a spacefill rendition showcased the proximity of the halide ligands to the *tert*-butyl substituents (Fig. 2). The overall steric encumbrance[8] of both the ^{nBu}TACN^{tBu} ligand and the halide were estimated via

solid-angle calculations.[9] For all Cu-X complexes, the $^{n\text{Bu}}$TACN$^{t\text{Bu}}$ ligand shields the metal center to a similar extent (67.2-67.4%). However, the metal-coordination-sphere shielding imparted by the halide (G_{halide}) is more variable and affords equivalent cone-angle (ECA) values of 105.19°, 103.13°, and 93.50°, for Br, I, and Cl, respectively, and contributes the greatest to differences in total ligand-coordination-sphere shielding (Fig. 2).[10] This M-X trend mirrors previous studies in high-valent chromium systems.[11]



	G_{halide}	ECA	T_c	$\Delta G^{\ddagger}$
1-Cl	15.7%	93.5°	-30 °C	11.1 kcal/mol
1-Br	19.6%	105.2°	-26 °C	11.3 kcal/mol
1-I	18.9%	103.1°	-20 °C	11.6 kcal/mol

Figure 2. Solid angle and variable-temperature ^{1}H NMR (CD_2Cl_2, 500 MHz) analysis of **1-X**. G_{halide} = Cu coordination sphere shielded by halide; ECA = equivalent cone angle; T_c = coalescence temperature; $\Delta G^{\ddagger}$ = activation energy barrier for *tert*-butyl rotation. Spacefill model of **1-I** derived from X-ray crystallography.

Diamagnetic complexes **1-X** display C_s symmetric ^{1}H NMR spectra ($CDCl_3$, 25 °C, 700 MHz) with a single, broad *tert*-butyl resonance where the full-width at half-max (fwhm) of this resonance follows the trend I > Br > Cl (15.8, 10.4, and 8.3 Hz, respectively). We hypothesized that the broad *tert*-butyl resonances are due to hindered rotation on the NMR timescale,[12] as a result of steric hindrance with the copper-coordinated halides. At 25 °C, each complex displays a well-defined singlet resonance near 1.3 ppm assigned as freely-rotating (symmetric) *tert*-butyl groups. Upon cooling, the *tert*-butyl resonance in each complex further broadens to coalescence temperatures between -20 to -30 °C (Figs. S12-S20). Further cooling reveals three new C*H*$_3$ resonances (6H each), consistent with hindered rotation of the *tert*-butyl (C_s symmetry is maintained). The activation energy barrier ($\Delta G^{\ddagger}$) for tert-butyl rotation was extracted from variable temperature ^{1}H NMR spectra (CD_2Cl_2, 500 MHz). These values range 11.1-11.6 kcal mol^{-1}, revealing minimal dependence upon the identity of the halide.

After clarifying the solution behavior of **1-X**, we examined requirements for cooperative binding interactions with ditopic substrates. One dibasic substrate of interest to our lab and others is hydrazine (N_2H_4).[3a, d, 13] Notably, few structurally-characterized Cu(I)-N_2H_4 complexes have been reported: there are six examples that feature one bound N_2H_4 molecule,[14] and only two that feature a single Cu site.[14c, d]

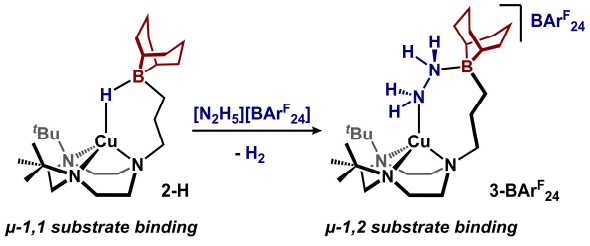


Figure 3. Flexibly appended Lewis acid accommodates μ-1,1 (**2-H**) and μ-1,2 (**3-BAr$^{F}_{24}$**) substrate binding modes.

To provide guidelines into the requirements needed to promote mononuclear cooperative binding with substrates at [(^{BBN}TACN$^{t\text{Bu}}$)Cu(I)], we targeted reactivity studies using (^{BBN}TACN$^{t\text{Bu}}$)Cu-H (**2-H**), a precursor amenable to protonation-induced ligand substitution. We previously demonstrated that boron-stabilized metal hydrides undergo ligand exchange with a Brønsted acid concomitant with elimination of H_2.[3e] When a thawing THF solution of **2-H** was treated with 1.0 equiv [N_2H_5][BAr$^{F}_{24}$], [(^{BBN}TACN$^{t\text{Bu}}$)Cu(N_2H_4)]$^+$ (**3-BAr$^{F}_{24}$**) formed in 71% yield (Fig. 3). The ^{1}H NMR spectrum of **3-BAr$^{F}_{24}$** revealed a single broad *tert*-butyl resonance (fwhm = 5.54 Hz; $CDCl_3$) consistent with rotational hindrance akin to **1-Cl**. Asymmetry of the N_2H_4 unit was apparent from the two broad NH_2 resonances (5.58 and 6.17 ppm; THF) and three prominent infrared absorbances (KBr; 3299, 3239, 3160 cm^{-1}). Interaction of the trialkylborane with the substrate was supported by ^{11}B NMR spectroscopy, which featured a resonance at -3.96 ppm (THF), consistent with a tetrahedral boron environment.[15] Importantly, these data support that the [(^{BBN}TACN$^{t\text{Bu}}$)Cu(I)] framework can accommodate both the μ-1,1 and μ-1,2 binding modes depending on the identity of the substrate..

Complex **3** is alternately accessible via direct addition of N_2H_4 to **2-OTf**, a variant which features a non-interacting appended trialkylborane. Treating a thawing THF solution of **2-OTf** with a 1.0 equiv. N_2H_4 furnished [(^{BBN}TACN$^{t\text{Bu}}$)Cu(N_2H_4)][OTf] (**3-OTf**) in 86% yield (Fig. 4). Following an XRD experiment, data refinement revealed a tetrahedral environment around Cu (τ_4 = 0.67) with a μ-1,2-N_2H_4 ligand bridging the Cu and the appended trialkylborane (ΣB_α = 321.13(8)°, B-N_2H_4 = 1.6521(13) Å). The Cu-N_2H_4 distance (2.0330(8) Å) is considerably shorter than the Cu-N_{TACN} distances (ave. = 2.2017 Å) by ~0.17 Å. Compared to complexes **1-X**, the equivalent cone angle for the N_2H_4 ligand in **4** is 102.30°, which most closely matches that of iodide in **1-I**. In the conversion from **2-H** to **3-OTf**, the flexibly appended borane moves 1.15 Å (with respect to copper) to accommodate the larger substrate. These results suggest that, in contrast to formate binding, the appended trialkylborane in **3-OTf** interacts with the terminal NH_2 of a N_2H_4 ligand within the same molecule, suggesting that μ-1,2-substrates may be ideally suited for cooperative interactions within the framework.

We sought to interrogate the requirement of the appended borane by employing ($^{n\text{Bu}}$TACN$^{t\text{Bu}}$)Cu(OTf) (**1-OTf**) which features the inert butyl group. Treating a thawing THF solution of **1-OTf** with a solution of 1.0 equiv. of N_2H_4 afforded the terminal N_2H_4 complex [($^{n\text{Bu}}$TACN$^{t\text{Bu}}$)Cu(N_2H_4)][OTf] (**4**) in 77% yield (Fig. 4a). The ^{1}H NMR spectrum of **4** revealed two broad NH_2 resonances at 3.61 and 4.78 ppm (CD_2Cl_2), consistent with asymmetric binding of the N_2H_4 moiety. The solid-state structure of **4** contains two molecules in the unit cell where N_2H_4 is terminally bound to a single copper (τ_4 = 0.69; Fig. 4c). Compared to **3-OTf**, the Cu–N_2H_4 distance in **4** (ave. = 1.986 Å) is shorter by ~0.05 Å. Although terminally bound, the N_2H_4 ligand engages in weak intermolecular hydrogen-bonding interactions with an adjacent molecule of **4** ($N\cdots H_{ave}$ = 2.3 Å, $N\cdots N_{ave}$ = 3.1 Å),[16] highlighting its preference for secondary binding interactions.

We investigated the hydrazine adducts in **3-OTf** and **4** computationally to compare the thermodynamics of hydrazine binding in each case. We employed density functional theory (DFT)

methods (B3LYP-D3/SVP (PCM = THF)). The binding of hydrazine to form a Cu-N_2H_4 complex is more favorable by ~6 kcal/mol when the appended borane is present (**3-OTf**) compared to when it is not (**4**), see SI. In addition to thermodynamic stabilization imparted by the appended Lewis acids, we examined the extent to which the Brønsted acidity of N_2H_4 is perturbed via Lewis acidic interactions, using DFT (Fig. 4b). Brønsted acidity can serve as a general proxy for substrate activation and, with hydrazine, may provide insight into acidification during PCET steps during N_2-to-NH_3 reduction. Complexes **3** and **4** were compared to a metal-free surrogate 9-propyl-9-borabicyclo[3.3.1]nonane (**9-Pr-9-BBN**), in analogy to a previous study with Zn-bound N_2H_4.[5a]

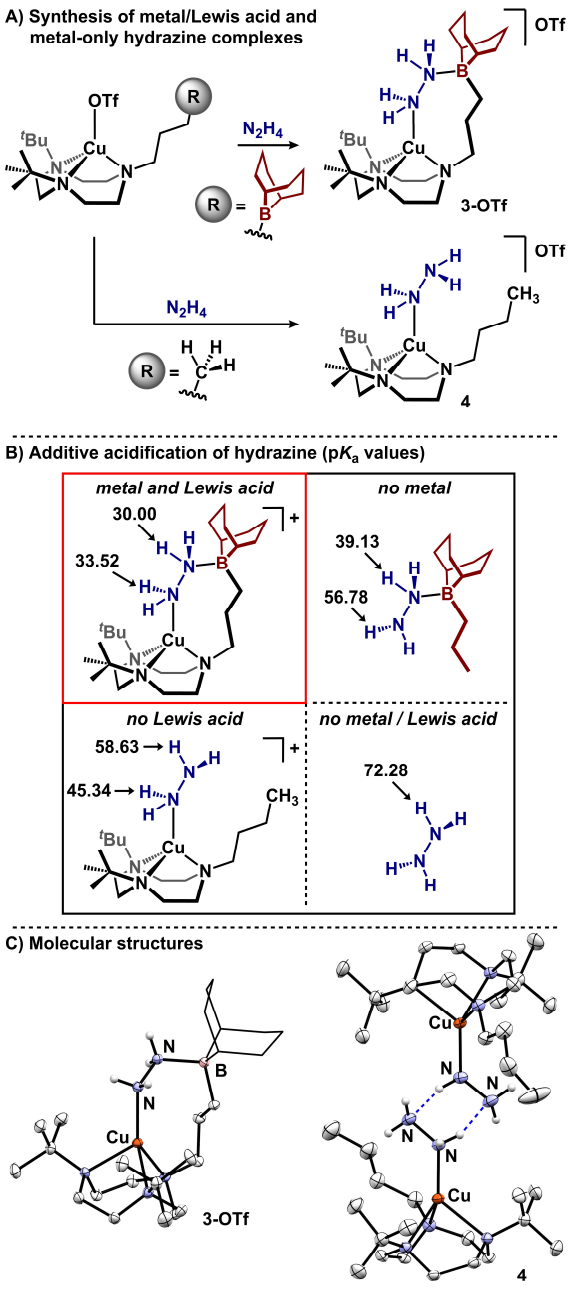


Figure 4. A) synthesis of **3-OTf** and **4**. B) Calculated pK_a values. C) Molecular structures of **3-OTf** and **4** displayed with 50% probability ellipsoids. H-atoms not attached to N_2H_4 and outer sphere triflate anions omitted for clarity.

For the hydrazine adduct of **9-Pr-9-BBN**, the proximal N-*H* protons are acidified by 33 pK_a units compared to unbound N_2H_4, while the distal protons are less influenced by Lewis acid binding (~15 pK_a units). A similar, though less pronounced, effect is observed for binding of N_2H_4 in **4**, with the proximal and distal N-*H* protons displaying pK_a values that are 27 and 14 units lower than free N_2H_4, respectively. Importantly, the dual interactions in **3** lead to Cu-N-*H* and B-N-*H* pK_a values that are considerably lower than those observed in the limiting cases (39 and 42 pK_a units lower than free N_2H_4, respectively), indicating that Cu(I) and the trialkylborane provide additive effects that acidify N_2H_4 to a greater extent.[5a] We sought to experimentally confirm this acidification in **3-OTf** via deprotonation of the bound N_2H_4. Unfortunately, addition of 1 equiv. base[18] to a thawing THF solution of **3-OTf** resulted in an intractable mixture (see SI for details). While no stable Cu-containing product was obtained, we found that when $KN(SiMe_3)_2$ was employed as the base, $HN(SiMe_3)_2$ was observed in the crude ^{1}H NMR spectrum, consistent with proton transfer, albeit without affording a stable metal-containing product.

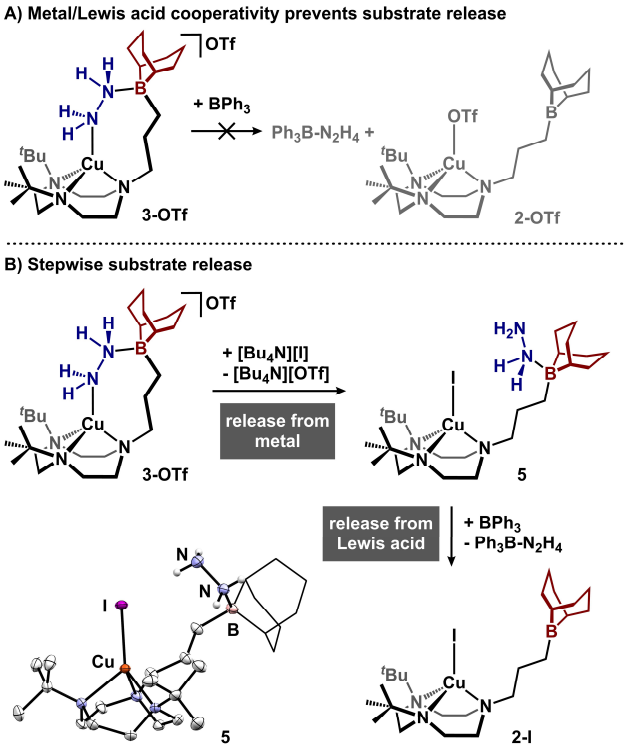


Figure 5. A) additive stabilization of hydrazine disallows substrate release. B) halting metal/Lewis acid cooperativity enables facile hydrazine release. Molecular structure of **5** (50% probability ellipsoids). H-atoms not connected to N_2H_4 are omitted and 9-BBN substituents displayed in wireframe.

Although irreversible binding of substrates (or reactive intermediates) is often the focus of reports detailing secondary sphere interactions, a requirement of any system to undergo turnover is the ability to undergo *release*; a product can sometimes feature a higher affinity for secondary sphere acidic groups than the substrate.[19] Given the ability of [(^{BBN}TACN^{tBu})Cu(I)] to stabilize both μ-1,2 and μ-1,1 substrates, we hypothesized this flexibility may facilitate substrate release. When **3-OTf** was treated with one equivalent of triphenylborane—a

more potent Lewis acid than a trialkylborane—no reaction occurred (Fig. 5A). The acceptor number of BPh_3 is 69 while that of an alkyl-BBN is 25, suggesting transfer between boranes, absent cooperativity with the metal, should be feasible.[5a, 20] This result highlights the additive effect of both the trialkylborane and copper(I) for sequestering hydrazine in analogy to the pK_a analysis. To enable hydrazine release, we first treated **3-OTf** with a competitive Lewis base, iodide, which cleaved the Cu-N_2H_4 interaction and formed (^{BBN}TACN^{tBu})CuI(N_2H_4) (**5**; Fig. 5B). X-ray diffraction confirmed the newly formed Cu-I bond (2.47402(16) Å) and that the borane operates independent of the metal to bind N_2H_4 (N-B = 1.6462(17) Å) with the terminal NH_2 lone-pair unquenched.[21] By first disrupting the cooperativity between copper and boron in forming **5**, hydrazine release is facile: triphenylborane readily abstracts hydrazine to generate Ph_3B-N_2H_4 and (^{BBN}TACN^{tBu})CuI (**2-I**).[22]

This study demonstrates that metal/Lewis acid cooperativity imparts additive effects for geometrically matched substrates both in terms of activation (pK_a) and substitutional stability. Both concepts can be employed for new avenues of substrate activation/functionalization and product exchange/extrusion to overcome catalyst inhibition encountered in catalytic processes. Current efforts are focused on extending these concepts to redox reactions using these and related substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Full experimental procedures and spectroscopic characterization of all species and crystal structure data (PDF).

Accession Codes

CCDC 2364703-2364712 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.

Notes

Appropriate safety protocols should be followed when using hydrazine.[23]

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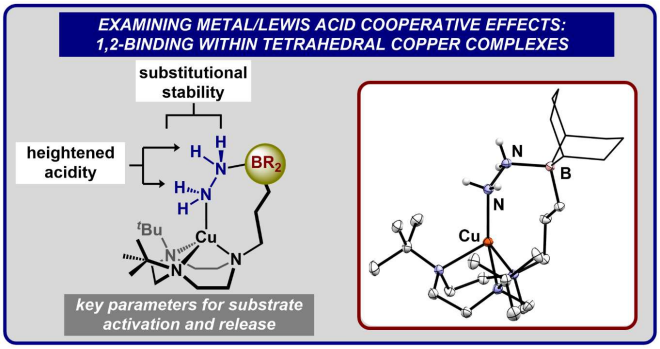

TOC Synopsis

Additive effects of metal/Lewis acid cooperativity are investigated in a Cu(I)-N_2H_4 complex featuring an appended trialkylborane. The cooperative stabilization of hydrazine by copper and the borane affords increased binding strength and activation (Brønsted acidity). In addition, hydrazine exchange with a competitive Lewis acid is only observed when the cooperative metal/Lewis acid interaction is first disrupted.