

# A Transition Metal Lewis Acid/Base Triad System for Cooperative Substrate Binding

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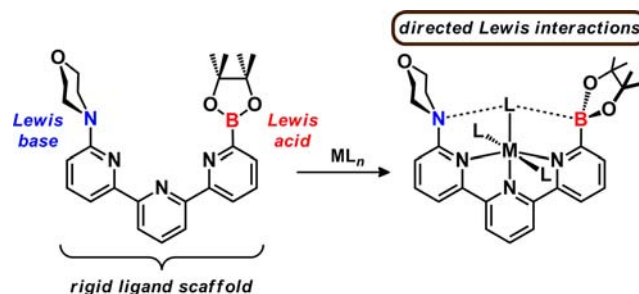
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**S** Supporting Information

**ABSTRACT:** A frustrated Lewis pair accessory functionality is positioned in the secondary coordination sphere of a terpyridine ligand (Tpy<sup>BN</sup> = 6-morpholino-2,2':6',2''-terpyridine-6''-boronic acid pinacol ester) to promote directed Lewis acid/base interactions. Following metalation with VCl<sub>3</sub>, the utility of the metal Lewis acid/base triad (LABT) is highlighted with N<sub>2</sub>H<sub>4</sub> as a cooperatively coordinated substrate, affording the first η<sup>2</sup>-[N<sub>2</sub>H<sub>3</sub>]<sup>-</sup> vanadium complex.

Metal–ligand cooperativity is a key feature of substrate activation by metalloenzymes, where well-ordered assemblies of metal cofactors and amino acid residues participate to promote specific chemical reactivity in enzyme active sites.<sup>1</sup> To replicate such function, synthetic model systems containing appended functionalities have been pursued, and many multifunctional ligand architectures have been shown to work in concert with a metal site for synergistic substrate binding/activation.<sup>2</sup> While the incorporation of Lewis acidic<sup>3</sup> or basic<sup>4</sup> groups have been explored, the placement of Lewis acidic and basic functionalities within a metal's secondary coordination sphere environment is particularly underdeveloped. Such frameworks offer enhanced capabilities for cooperative substrate activation since multiple points of contact for coordination are provided; redox transformations may also be facilitated through metal-mediated electron transfer.

We are working to develop key design principles that dictate tenets by which transition metal complexes can work in concert with their secondary coordination sphere environment.<sup>5</sup> Metal-free systems that bind small molecules were recently developed that incorporate highly potent Lewis acid/base pairs.<sup>6</sup> The so-called frustrated Lewis pairs (FLPs) form adducts with substrates such as CO<sub>2</sub><sup>7</sup> and N<sub>2</sub>O,<sup>8</sup> demonstrating that cooperative binding of typically inert substrates is possible. We sought to couple the Lewis acid/base strategy with a transition metal fragment to enable synergistic binding of substrates in atypical binding modes and/or to facilitate further redox transformations. We targeted a ligand framework that when appropriately decorated would place appended Lewis acid/base functionalities in close proximity to the substrate binding site (Figure 1). Further aspects of our design criteria included (1) a rigid structure to prevent (a) coordination of the Lewis base to the metal center and (b) acid–base adduct formation and (2) a modular synthetic route permitting appropriate tuning of the acidity/basicity of the pendent groups.



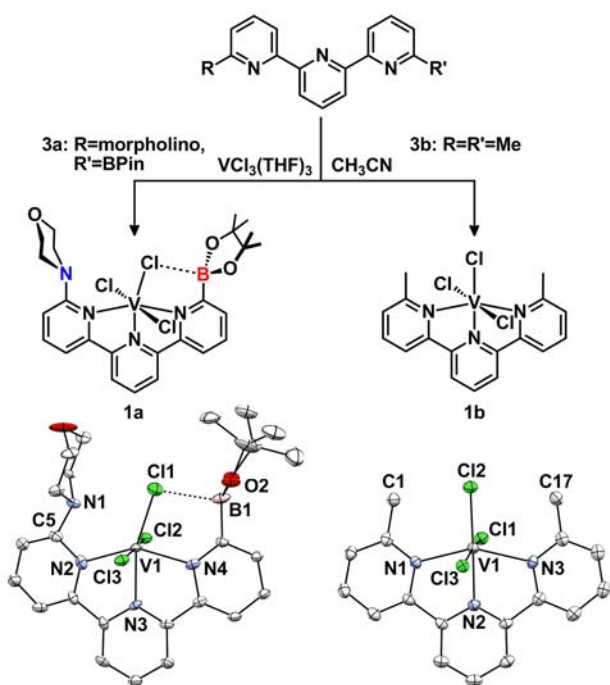
**Figure 1.** The Lewis acid/base-appended pincer ligand used in this study, Tpy<sup>BN</sup> (3a), including the key design criteria.

A scaffold based on the 2,2':6',2''-terpyridine (Tpy) ligand was selected to satisfy the above requirements. Pincer complexes incorporating the Tpy ligand platform are sufficiently rigid that adjacent Lewis acid/base pairs placed at the Tpy 6 and 6'' positions cannot form an intramolecular adduct. Furthermore, because the central pyridine ring can be constructed at the final stage of the synthesis,<sup>9</sup> this ligand class lends itself to a modular design to accommodate alternative Lewis acid/base partners. Our design targeted a system that contains a boronic ester and a morpholine group as weakly Lewis acidic and Lewis basic partners, respectively, in order to impart moderate assistance from the metal's secondary coordination sphere environment. The asymmetric terpyridine ligand 3a (Tpy<sup>BN</sup>) was synthesized by a convergent pathway in which the central ring was generated by Kröhnke condensation of derivatives of *o*-morpholinopyridine and *o*-bromopyridine to afford 6-bromo-6''-morpholino-2,2':6',2''-terpyridine. The Lewis acidic pinacol boronic ester was installed in the last step via Pd-mediated Miyaura coupling.<sup>10</sup>

To examine the structural features of the Tpy<sup>BN</sup> ligand, we first prepared its vanadium(III) complex by allowing equimolar amounts of Tpy<sup>BN</sup> and [VCl<sub>3</sub>(THF)<sub>3</sub>] to react in acetonitrile for 3 h under an inert atmosphere, which afforded [V(Tpy<sup>BN</sup>)-Cl<sub>3</sub>] (1a) as an orange solid in high yield (93%; Figure 2). We sought to evaluate directly the structural and electronic parameters imposed by the polarized secondary coordination sphere environment, and thus, we also prepared Tpy<sup>Me<sub>2</sub></sup> (3b), a structurally similar complex with methyl substituents at the 6 and 6'' positions (Figure 2).<sup>11</sup> The synthesis of 1b proceeded analogously to that of 1a, and the complex was obtained as an orange solid in 96% yield. Both 1a and 1b are paramagnetic,

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**Figure 2.** Molecular structures of (left) **1a** and (right) **1b** with ellipsoids drawn at 50% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1a**: V1–Cl1, 2.292(2); V1–Cl2, 2.340(2); V1–Cl3, 2.363(2); V1–N2, 2.126(6); V1–N3, 2.104(4); V1–N4, 2.158(6); N2–V1–Cl1, 125.0(2); Cl1–V1–N4, 86.9(2). For **1b**: V1–Cl2, 2.3274(8); V1–Cl1, 2.3196(7); V1–Cl3, 2.3956(7); V1–N1, 2.194(2); V1–N2, 2.072(2); V1–N3, 2.212(2); N1–V1–Cl2, 104.35(6); Cl2–V1–N3, 103.90(6).

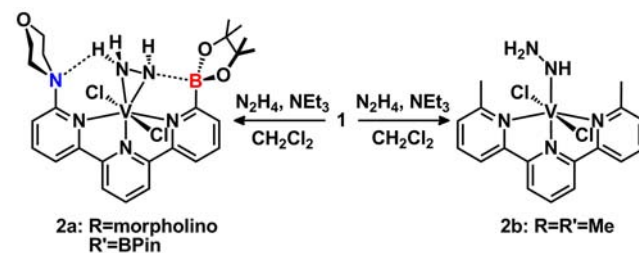
with magnetic moments of  $2.59\mu_B$  and  $2.63\mu_B$ , respectively, which supports a  $d^2$  V(III) electron configuration. Consistent with coordination of the Tpy framework to the vanadium center, both compounds exhibit distinct paramagnetically shifted  $^1\text{H}$  NMR resonances, and the  $^{11}\text{B}$  NMR resonance of **1a** is shifted upfield by ca. 70 ppm relative to the free ligand **3a**. The electronic differences in the ligand fields presented to vanadium in the two ligand systems were assessed by electrochemical studies. Three redox processes were observed cathodic of the open-circuit potential for **1a**, while two were noted for **1b** (Figures S5–S9 in the Supporting Information).<sup>12</sup> The first reduction process for both **1a** and **1b** is quasi-reversible, with  $E_{1/2}$  values of 0.50 and 0.55 V vs SCE, respectively. This was assigned to a  $\text{V}^{\text{III/II}}$  reduction event, consistent with prior results for vanadium complexes with similar ligand fields.<sup>13</sup> The similarity of the redox potentials ( $\Delta E_{1/2} = 0.05$  V) suggests that the ligand fields provided by **3a** and **3b** are similar despite the modification of the 6 and 6'' pendent groups.

Crystals of **1a** and **1b** suitable for X-ray analysis were obtained by slow diffusion of  $\text{Et}_2\text{O}$  into  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{Cl}_2/\text{N,N}$ -dimethylacetamide solutions, respectively.<sup>14</sup> Comparative analyses of their solid-state structures revealed distinct primary coordination geometries around vanadium (Figure 2). Both complexes feature a distorted octahedral geometry about vanadium, but in the structure of **1a**, an axial chloride ligand is bent toward the boronic ester group, as illustrated by the Cl1–V1–N3 angle of  $162.0(2)^\circ$ . Furthermore, the B1–Cl1 distance of  $2.410(9)$  Å is consistent with a B–Cl interaction. Similar M–Cl→B interactions have been described with alkyl-

and arylboranes,<sup>15</sup> for which shorter B–Cl distances (1.980–2.166 Å) have been reported, consistent with increased Lewis acidity on boron.<sup>16</sup> In support of the weak M–Cl→B interaction in **1a**, the degree of pyramidalization at boron is relatively low [ $\sum B_\alpha = 349.8(12)^\circ$ ].<sup>15</sup> A close-contact interaction between the morpholino nitrogen (N1) and vanadium [V1–N1 =  $2.79(2)$  Å] also exists, which concomitantly decreases the N1–C5–N2 bond angle [ $102.7(8)^\circ$ ]. The ability of the secondary coordination sphere environment in **1a** to modify the primary-coordination chloride binding site was confirmed by comparison with the solid-state structure of **1b**, which contains methyl groups in place of the BPin and  $\text{NR}_2$  moieties (Figure 2). The  $\text{VCl}_3$  fragment in **1b** is distorted ca.  $23^\circ$  out of the Tpy plane (Figure S14), while the axial chloride ligand is roughly equidistant from the two methyl groups, in stark contrast to the  $\text{VCl}_3$  arrangement in **1a**.

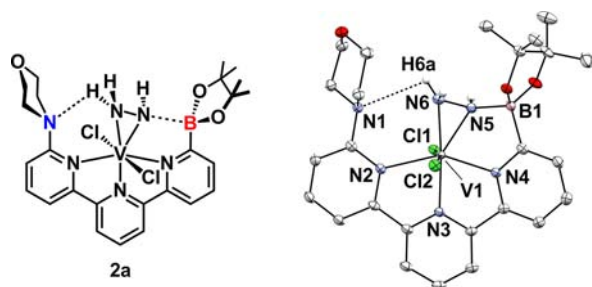
To demonstrate the utility of the appended Lewis functional groups for cooperative substrate interactions, we explored the reactivity of **1a** with hydrazine, a substrate that can interact with both the pendent Lewis acid and base when bound to the metal. Furthermore, vanadium complexes with nitrogenous ligands are potentially relevant to the catalytic site of V-nitrogenase, whose structure remains elusive yet likely incorporates a multimetallic core consisting of multiple Lewis acidic sites and nearby amino acid residues for  $\text{N}_2$  activation.<sup>17</sup> Upon addition of  $\text{N}_2\text{H}_4$  to a  $\text{CH}_2\text{Cl}_2$  solution of **1a** in the presence of 5 equiv of  $\text{NEt}_3$ , **2a** precipitated as a maroon solid in 71% yield (Scheme 1). Complex **2a** is paramagnetic, with a

#### Scheme 1. Reactions of **1a** and **1b** with Hydrazine in the Presence of $\text{NEt}_3$



magnetic moment of  $2.73\mu_B$ , consistent with retention of a V(III) oxidation state. The  $\text{N}_2\text{H}_x$  unit of **2a** was interrogated with IR spectroscopy, which revealed three N–H stretching bands at 3300, 3249, and  $3204\text{ cm}^{-1}$ , consistent with a hydrazido ( $\text{N}_2\text{H}_3^-$ ) ligand.<sup>18</sup>

Red crystals of **2a** suitable for X-ray analysis were obtained by slow diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_2\text{Cl}_2$  solution. The solid-state structure of **2a** reveals an unusual  $\eta^2$  coordination mode of  $\text{N}_2\text{H}_3^-$  to V(III) supported by both Lewis acidic and Lewis basic interactions (Figure 3). The N5–N6 bond length is  $1.391(3)$  Å, which is modestly contracted relative to that in the parent hydrazine<sup>19</sup> and in agreement with those in previously reported unsubstituted  $\eta^2$ -hydrazido(1–) complexes.<sup>18,20</sup> The vanadium center in **2a** retains two trans-disposed  $\text{Cl}^-$  ligands and exhibits a distorted octahedral coordination geometry. The H atoms of the hydrazido ligand were located from the difference map, affording a structure consistent with the assignment of a charge-neutral V(III) complex. As noted above, the  $\text{N}_2\text{H}_3^-$  unit participates in close-contact interactions with both of the appended Lewis acid and Lewis base functional groups. For instance, H6A exhibits intramolecular



**Figure 3.** Molecular structure of **2a**. Displacement ellipsoids are drawn at 50% probability, and H atoms except N–H have been omitted for clarity. Selected bond lengths (Å): V1–Cl1, 2.4219(7); V1–Cl2, 2.4102(7); V1–N2, 2.261(2); V1–N3, 2.104(2); V1–N4, 2.113(2); V1–N5, 2.035(2); V1–N6, 2.060(2); N6–N5, 1.391(3); N5–B1, 1.623(4).

hydrogen bonding to N1 of the morpholino group [H6A–N1 = 2.68(4) Å, N1–N6 = 2.990(3) Å]. Also, the adjacent N atom (N5) engages in a bonding interaction with B1 of the appended boronic ester with a B1–N5 distance of 1.623(4) Å, consistent with an elongated single bond<sup>21</sup> and longer than the values reported for the related complexes [(SiP<sup>iPr</sup><sub>3</sub>)Fe<sup>II</sup>(N<sub>2</sub>H<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>)] (ca. 1.548 Å) and [Ti(N<sub>2</sub>N<sup>Pr</sup>){η<sup>2</sup>-N-(NPh<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}] (1.598 Å).<sup>22,23</sup>

Notably, there are few structurally characterized examples of transition metal complexes of the unsubstituted η<sup>2</sup>-hydrazido(1–) ligand,<sup>18,20</sup> and to the best of our knowledge, no structurally characterized complexes featuring η<sup>2</sup> coordination of N<sub>2</sub>H<sub>3</sub><sup>–</sup> or N<sub>2</sub>H<sub>4</sub> to vanadium have been reported.<sup>24</sup> Thus, complex **2a** represents a unique binding mode of a N<sub>2</sub>H<sub>4</sub><sup>–</sup> derived ligand to a monometallic vanadium complex, with potential relevance to intermediates involved in synthetic N<sub>2</sub> reduction cycles.

In contrast to the reactivity observed with **1a** and hydrazine, **1b** reacted with hydrazine under identical conditions to give a distinct product, **2b**. The reaction stoichiometry was identical, as confirmed by the reactions of **1b** with an equimolar amount of N<sub>2</sub>H<sub>4</sub> in the presence and absence of exogenous base. Without added base, **2b** was obtained in 50% yield, while a quantitative yield was realized upon addition of 5 equiv of NEt<sub>3</sub>. We were unable to obtain X-ray-quality single crystals of **2b**, which precluded crystallographic analysis; however, comparative spectroscopic characterization of **2a** and **2b** revealed stark differences. For instance, the IR spectrum of **2b** contains two sharp N–H bands at 3344 and 3248 cm<sup>–1</sup>, in contrast to the three N–H bands noted for **2a**. Voltammetric studies illuminated further differences between **2a** and **2b** (Figures S12 and S13, respectively) by comparison with their corresponding VCl<sub>3</sub> adducts, **1a** and **1b**.<sup>25</sup> Three well-defined quasi-reversible reduction events are present for **2a**, which are shifted ca. 500 mV to more cathodic potentials than for **1a**. The cathodic shift is consistent with the change in coordination environment upon replacement of an X-type axial chloride ligand by an LX-type η<sup>2</sup>-coordinated hydrazido(1–) ligand.<sup>20d</sup> In contrast, two reduction processes were observed for **2b**, occurring at potentials similar to those for its precursor **1b**; this is consistent with minor changes in the ligand field of the axially coordinated unit, as expected upon modification of a π-donor, X-type ligand (i.e., changing a Cl<sup>–</sup> for an η<sup>1</sup>-NHNH<sub>2</sub><sup>–</sup> ligand). Thus, **2b** is tentatively assigned to contain a terminal NHNH<sub>2</sub><sup>–</sup> ligand (Scheme 1). Several accounts of terminal hydrazido(1–) complexes have also reported two N–H stretching bands,

consistent with our observations.<sup>26</sup> Although alternative coordination modes of hydrazine (e.g., an [NHNH]<sup>2–</sup> bridged dimer) would also be consistent with the spectroscopic data,<sup>27</sup> elemental analysis unambiguously dismissed a dimeric formulation.<sup>10</sup>

Hydrazine has been observed as a byproduct of N<sub>2</sub> reduction to ammonia by V-nitrogenase, and thus, vanadium complexes of N<sub>2</sub>H<sub>3</sub><sup>–</sup> and N<sub>2</sub>H<sub>4</sub> represent possible intermediate structures along a vanadium-mediated N<sub>2</sub> reduction pathway.<sup>28</sup> Accordingly, the relative ability of **2a** and **2b** to mediate N<sub>2</sub>-centered redox transformations was examined. Electrochemical experiments were used to guide chemical redox studies; the quasi-reversible reduction wave at –1.25 V vs SCE displayed by **2a** in *N,N*-dimethylformamide (DMF) suggested [CoCp\*<sub>2</sub>] as an appropriate reductant. When treated with [CoCp\*<sub>2</sub>], and collidinium hydrochloride, **2a** furnished 0.6 ± 0.2 equiv of NH<sub>3</sub> as determined by the indophenol colorimetric assay,<sup>29</sup> consistent with reduction-induced N–N bond cleavage. The yield of ammonia increased to 1.8 ± 0.2 equiv when the reduction was performed in the presence of 10 equiv of N<sub>2</sub>H<sub>4</sub>, suggesting that a ligand substitution reaction is kinetically competent under the reaction conditions.<sup>30</sup> Control reactions confirmed that no ammonia was formed in the absence of **2a**, which supports a V-mediated hydrazine reduction.

In summary, this communication demonstrates a new Lewis triad system that uses a terpyridine-based ligand framework bearing Lewis acid and Lewis base groups (**3a**) to direct secondary coordination sphere interactions. Of particular note, when **3a** was metalated with V(III), significant interactions with the ligand trans to the central pyridine ring were noted for **1a** and **2a**. Comparison with the sterically similar compounds **1b** and **2b** containing methyl substituents in place of the Lewis acidic and basic groups illustrates the ability of the secondary coordination sphere to participate cooperatively in binding small molecules such as N<sub>2</sub>H<sub>3</sub><sup>–</sup>. The Lewis acid/base-appended ligand set represents the first well-defined example of a ligand framework that enforces highly directed Lewis acid/base interactions with a metal-coordinated substrate. Work is ongoing to extend the utility of metal–ligand constructs containing **3a** and similar Lewis triads to a variety of small-molecule transformations as well as to induce further oxidative transformations of **2a** to generate N<sub>2</sub> and/or diazene-type species.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental procedures, spectroscopic and electrochemical data, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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