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Nitrogen Fixation

Azo N=N Bond Cleavage with a Redox-Active Vanadium Compound Involving Metal–Ligand Cooperativity**

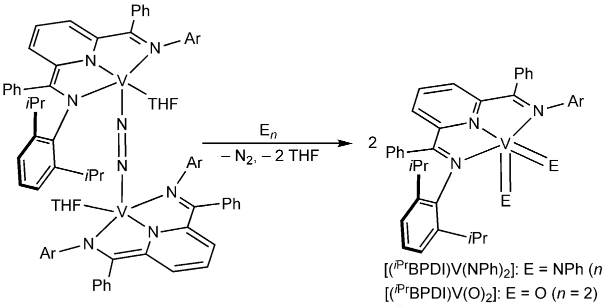
Carsten Milsmann, Zoë R. Turner, Scott P. Semproni, and Paul J. Chirik*

The cleavage of N−N bonds by soluble transition metal complexes is of interest for understanding the mechanisms of nitrogen fixation and for the possibility of developing new transformations that utilize molecular nitrogen, azo compounds and hydrazines as N-atom or [NR_n] ($n = 1,2$) group sources.[1] Accomplishing these objectives with well-defined, molecular vanadium compounds is motivated by the role of vanadium in nitrogenase enzymes[2] and precedent in synthetic compounds for ammonia synthesis[3] and N_2 cleavage.[4] Scission of related RN=NR and $R_2N{-}NR_2$ bonds is also mechanistically significant in understanding N_2 fixation schemes and offers potential value in catalytic and stoichiometric transformations involving [NR] or [NR_2] transfer.

Metal complexes with redox-active ligands, those that engage in reversible electron transfer with the metal,[5] offer intriguing opportunities for small-molecule activation and functionalization as metal–ligand cooperativity may lower kinetic barriers and enable unique reaction chemistry.[6] Heyduk has pioneered this concept in early transition metal chemistry and demonstrated a rich and unusual reaction chemistry of metal imido complexes with redox-active supporting ligands.[6b] Aryl-substituted bis(imino)pyridines are attractive for this purpose due to their synthetic accessibility, modularity,[7] well-established redox-activity[8] and precedent for supporting catalytically active base metal complexes.[9] Most relevant to nitrogen functionalization is the observation that bis(imino)pyridine iron imide complexes,[10] [(^{iPr}PDI)FeN*Ar*] (^{iPr}PDI = 2,6-(2,6-iPr$_2$-C_6H_3N=CMe)$_2$$C_5H_3N$; Ar = 2,6-R_2-C_6H_3, R = Et, iPr), when exposed to 1 atm of H_2 at 23 °C undergo rare examples of complete hydrogenolysis of a metal–nitrogen bond.[11] Inspired by these observations, we sought to prepare potentially more reducing early transition metal analogs to exploit metal–ligand cooperativity in reactions relevant to nitrogen fixation. Here we describe progress toward this objective with the observation of azo N=N bond cleavage with a reduced bis(imino)pyridine vanadium dinitrogen complex. This reactivity also includes the cleavage of O_2 and elemental sulfur to yield vanadium dioxo and disulfide compounds, respectively. Evaluation of the electronic structures of the reactants and products established that the overall four-electron reduction of substrate occurs using electrons stored in the bis(imino)pyridine chelate, coordinated dinitrogen and the vanadium center. This serves to highlight the potential of metal–ligand cooperativity in small-molecule activation processes.

Bis(imino)pyridine vanadium dinitrogen chemistry was pioneered by Gambarotta and co-workers with the synthesis of [{(^{iPr}PDI)V(THF)}$_2$(μ_2-N_2)] from addition of excess NaH to [(^{iPr}PDI)VCl_3] under an N_2 atmosphere.[12,13] As is well-documented in bis(imino)pyridine chemistry,[13,14] C−H bond activation of the imine methyl groups can be competitive with reduction of the metal complex and a second vanadium end-on dinitrogen complex with a modified chelate has been isolated under different conditions. To protect against these side reactions, our studies commenced with the preparation of [(^{iPr}BPDI)VCl_3] (^{iPr}BPDI = 2,6-(2,6-iPr$_2$-C_6H_3N=CPh)$_2$-C_5H_3N)[15] where the imine methyl groups have been replaced with phenyl substituents. Reduction with excess 0.5 % sodium amalgam in diethyl ether for 1 h followed by addition of THF and subsequent recrystallization furnished dark green crystals identified as [{(^{iPr}BPDI)V(THF)}$_2$(μ_2-N_2)]. As reported for [{(^{iPr}PDI)V(THF)}$_2$(μ_2-N_2)],[13] the vanadium dinitrogen compound is paramagnetic and NMR silent. The solid-state structure, presented in the Supporting Information, establishes the expected dimeric vanadium compound with terminal THF ligands and a bridging, end-on dinitrogen molecule. The N−N bond distance of 1.232(2) Å and the distortions to the bis(imino)pyridine chelates, which signal two-electron reduction,[8] establish vanadium(III) centers as originally suggested by Gambarotta for [{(^{iPr}PDI)V(THF)}$_2$(μ_2-N_2)].[13]

To explore the potential for N=N bond cleavage, a diethyl ether solution of [{(^{iPr}BPDI)V(THF)}$_2$(μ_2-N_2)] was treated with one equivalent of azobenzene at 20 °C and furnished the bis(imino)pyridine bis(imide) complex as dark brown crystals



(1)

[{(^{iPr}BPDI)V(THF)}$_2$(μ_2-N_2)]

[(^{iPr}BPDI)V(NPh)$_2$]: E = NPh (n = 2)
[(^{iPr}BPDI)V(O)$_2$]: E = O (n = 2)
[(^{iPr}BPDI)V(S)$_2$]: E = S (n = 8)

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[*] C. Milsmann, Z. R. Turner, S. P. Semproni, Prof. P. J. Chirik
Department of Chemistry, Princeton University
292 Frick Laboratory, Princeton, NJ 08544 (USA)
E-mail: pchirik@princeton.edu

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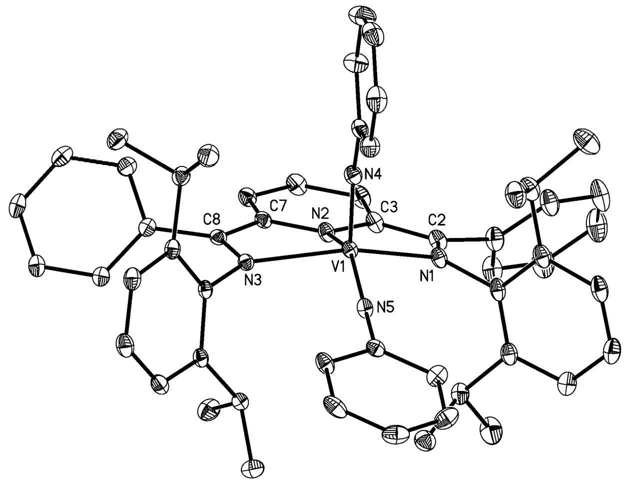


Figure 1. Representation of the solid-state structure of $[(^{iPr}\text{BPDI})\text{V(NPh)}_2]$ at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

in 69% yield [Eq. (1)]. The solid-state structure of $[(^{iPr}\text{BPDI})\text{V(NPh)}_2]$ is presented in Figure 1 and selected bond lengths and angles are reported in Table 1. The V-N_{imide} distances of 1.6986(17) and 1.7108(16) Å are as expected for vanadium imidos and the bond distortions in the bis(imino)pyridine chelate are consistent with one electron reduction[8] and hence a $[\text{BPDI}]^{\bullet-}$ radical anion.

Table 1: Selected bond lengths [Å] and angles [deg] for $[(^{iPr}\text{BPDI})\text{V(E)}_2]$ and $[\{(^{iPr}\text{BPDI})\text{V(Se)}\}_2(\mu_2\text{-Se}_2)]$.

E	NPh	O	S	Se
V–E	1.6986(17)	1.6240(15)	2.0731(7)	2.2273(5)
	1.7108(16)	1.6205(15)	2.0946(6)	2.3495(5)
				2.2148(5)
				2.3897(5)
C_{im}–N_{im}	1.329(3)	1.321(3)	1.326(3)	1.333(3)
	1.321(2)	1.326(3)	1.318(3)	1.331(3)
				1.349(3)
				1.334(3)
C_{im}–C_{ip}	1.438(3)	1.453(3)	1.446(3)	1.437(3)
	1.448(3)	1.447(3)	1.444(3)	1.430(4)
				1.436(4)
				1.444(4)
C_{ip}–N_{py}	1.367(3)	1.367(3)	1.364(3)	1.377(3)
	1.369(2)	1.368(3)	1.365(3)	1.372(3)
				1.369(4)
				1.372(3)

Examples of vanadium bis(imido) compounds,[16] particularly those prepared from azo N=N bond cleavage, are rare. Kawaguchi and co-workers[17] reported that treatment of a tris(arylthiolate)vanadium(III) complex with PhN=NPh resulted in azo N=N bond cleavage and yielded a product with a terminal imido ligand and a sulfenamide ligand arising from concomitant S–N bond formation. Tsai and co-workers[18] observed azo N=N bond cleavage to form a β-diketiminate vanadium bis(imido) following addition of PhN=NPh to an inverted toluene sandwich derivative. One related and more unique example has been reported by Mindiola and co-workers, where treatment of a [PNP] pincer-ligated vanadium bis(telluride) compound with $^1\text{AdN}_3$ (^{1}Ad = 1-adamantyl) furnished the corresponding bis(imido) with extrusion of elemental Te.[19]

The observation of facile N=N bond cleavage with azobenzene prompted exploration of similar four-electron bond activation reactions with the Group 16 elements. Exposure of a toluene solution of $[\{(^{iPr}\text{BPDI})\text{V(THF)}\}_2(\mu_2\text{-N}_2)]$ to two equivalents of O_2 at 20 °C resulted in immediate formation of a red solution which yielded, following recrystallization from pentane at −35 °C, the bis(imino)pyridine vanadium bis(oxide) $[(^{iPr}\text{BPDI})\text{V(O)}_2]$ [Eq. (1)]. This paramagnetic, NMR-silent product was also obtained in 86% yield following treatment of a toluene solution of $[\{(^{iPr}\text{BPDI})\text{V(THF)}\}_2(\mu_2\text{-N}_2)]$ with four equivalents of N_2O.

An analogous vanadium product was obtained from elemental sulfur. Addition of a toluene solution of $[\{(^{iPr}\text{BPDI})\text{V(THF)}\}_2(\mu_2\text{-N}_2)]$ to solid S_8 followed by stirring at 20 °C and recrystallization at −35 °C yielded the bis(sulfido) compound, $[(^{iPr}\text{BPDI})\text{V(S)}_2]$, as a paramagnetic, NMR-silent brown solid in 66% yield [Eq. (1)]. Both $[(^{iPr}\text{BPDI})\text{V(O)}_2]$ and $[(^{iPr}\text{BPDI})\text{V(S)}_2]$ were characterized by X-ray diffraction, and representations of the solid-state structures are presented in Figure 2 confirming formation of monomeric bis(imino)pyridine vanadium bis(chalcogenido) compounds. The metrical parameters of the chelates, reported in Table 1, are diagnostic of one-electron reduction[8] and formation of a $[\text{BPDI}]^{\bullet-}$ radical anion.

Efforts to prepare the selenium analog produced a slightly different outcome. Addition of excess gray selenium to

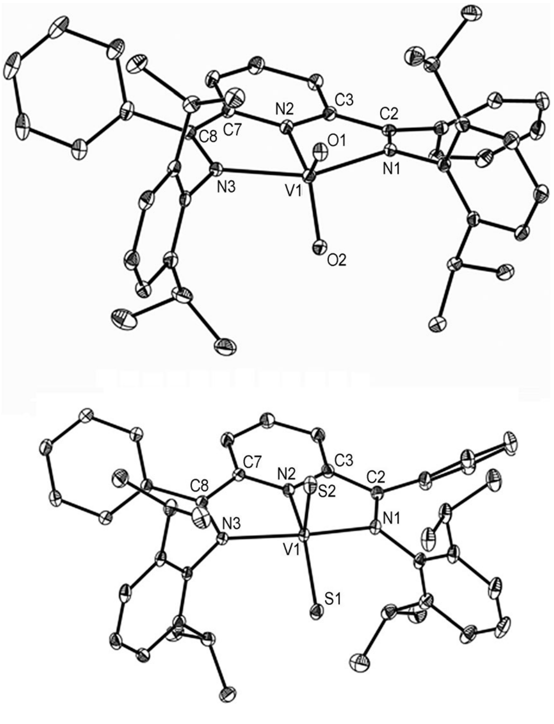
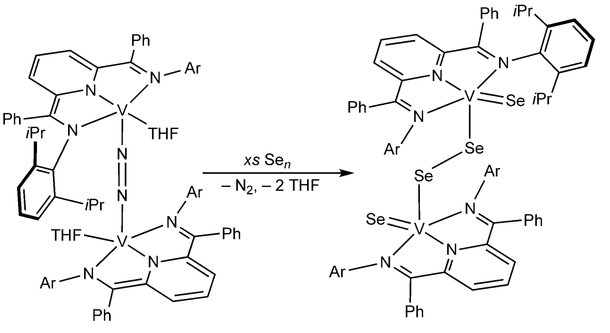


Figure 2. Representations of the solid state structures of $[(^{iPr}\text{BPDI})\text{V(O)}_2]$ and $[(^{iPr}\text{BPDI})\text{V(S)}_2]$ at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.



$[\{(^{iPr}BPDI)V(THF)\}_2(\mu_2\text{-}N_2)]$ $[\{(^{iPr}BPDI)V(Se)\}_2(\mu_2\text{-}Se_2)]$ (2)

a toluene solution of $[\{(^{iPr}BPDI)V(THF)\}_2(\mu_2\text{-}N_2)]$ followed by filtration and recrystallization from a toluene/pentane mixture at −35 °C furnished diamagnetic dark brown crystals in 85 % yield [Eq. (2)]. X-ray diffraction analysis (Figure 3) established formation of a dimeric bis(imino)pyridine vanadium compound each with a terminal selenido ligand bridged by a $[\mu_2\text{-Se}]^{2-}$ ligand. The ligand bond distances clearly indicate $[BPDI]^{\bullet-}$. The ^1H NMR chemical shifts are consistent with a diamagnetic compound. To our knowledge, this terminal selenide, μ_2-perselenido motif is unprecedented.

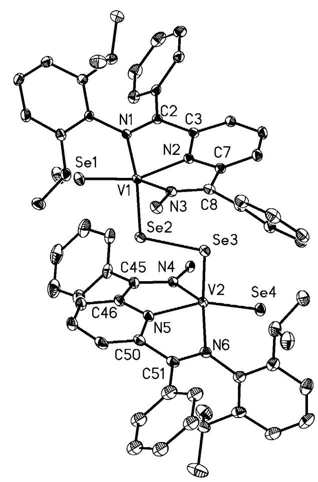


Figure 3. Representation of the solid state structure of $[\{(^{iPr}BPDI)V(Se)\}_2(\mu_2\text{-}Se_2)]$ at 30 % probability ellipsoids. Hydrogen atoms and two *i*Pr substituents omitted for clarity.

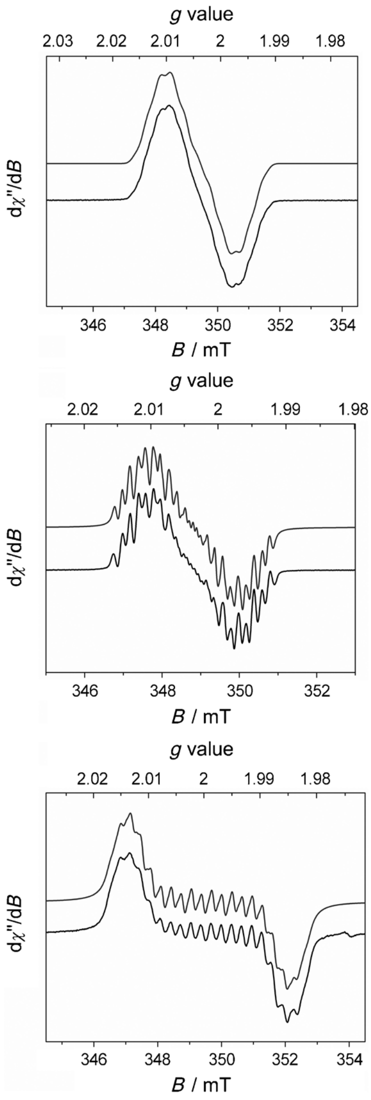


Figure 4. Experimental (black) and simulated (gray) toluene solution EPR spectra of $[(^{iPr}BPDI)V(NPh)_2]$ (top), $[(^{iPr}BPDI)VN(O)_2]$ (middle), and $[(^{iPr}BPDI)V(S)_2]$ (bottom) recorded at 23 °C. Power 2.0 mW, modulation 0.02 mT/100 kHz. Simulations were obtained with the parameters specified in Table 1.

Formation of $[(^{iPr}BPDI)V(E)_2]$ (E = NPh, O, S) products from azo N=N bond cleavage or from the Group 16 elements raised the question as to the source of the reducing equivalents and the role of the bis(imino)pyridine chelate in the bond activation chemistry. Accordingly, a more detailed investigation into the electronic structures of this family of compounds was carried out. EPR spectra were recorded to probe the orbital parentage of the unpaired spins. The toluene solution EPR spectra of $[(^{iPr}BPDI)V(E)_2]$ recorded at 23 °C (Figure 4) exhibit isotropic signals diagnostic of molecules with an $S = 1/2$ ground state.[21] Simulations of the data established g values of 2.003, 2.004 and 1.999 for $[(^{iPr}BPDI)V(NPh)_2]$, $[(^{iPr}BPDI)V(O)_2]$ and $[(^{iPr}BPDI)V(S)_2]$, respectively, consistent with principally organic radicals. The spectra for the chalcogenido compounds show well-resolved hyperfine couplings (HFCs) and were readily simulated including contributions from vanadium (^{51}V, $I = 7/2$), the BPDI nitrogen atoms ($^{14}N_{py}$ and $2\,^{14}N_{im}$, $I = 1$), and pyridine protons ($^1H_{para}$ and $2\,^1H_{meta}$, $I = 1/2$) using the parameters reported in Table 2.

The spectrum of $[(^{iPr}BPDI)V(NPh)_2]$ exhibits a much broader line width, which is most likely due to additional small HFC contributions from the two imido nitrogen atoms. As a result, the HFC could not be well resolved experimentally. Nevertheless, the HFC parameters obtained from DFT calculations (see below) result in a satisfactory fit of the data. Similar spectral features have been reported by Gambarotta and co-workers for $[(^{iPr}PDI)AlMe_2]$ and were key in establishing an Al^{III} compound with a bis(imino)pyridine radical anion, $[PDI]^{\bullet-}$, as the SOMO.[22] By way of calibration, typical

Table 2: EPR *g*- and *A*-values [MHz] determined from spectral fitting and DFT calculations.[a,b]

	$[(^{iPr}BPDI)V(NPh)_2]$		$[(^{iPr}BPDI)V(O)_2]$		$[(^{iPr}BPDI)V(S)_2]$	
	Sim.	Calcd.	Sim.	Calcd.	Sim.	Calcd.
g_{iso}	2.003	2.003	2.004	2.003	1.999	1.999
$A_{iso}(^{51}V)$	8	−11.59	8.0	−12.33	17.8	−16.53
$A_{iso}(^{14}N_{py})$	11	11.11	10.7	9.82	9.2	9.45
$A_{iso}(^{14}N_{im})$	6	5.95	5.3	5.84	4.3	4.28
$A_{iso}(^{1}H_{para})$	10	−9.79	12.8	−12.35	9.5	−10.06
$A_{iso}(^{1}H_{meta})$	1	3.38	1.2	4.08	1.2	3.59

[a] Simulated values are reported as absolute values. [b] Simulated values are rounded based on spectral resolution.

^{51}V hyperfine values in d^1 compounds are on the order of 200–300 MHz.[21] Therefore, our analysis of the BPDI HFC in $[(^{iPr}BPDI)V(E)_2]$ supports the assignment as principally ligand-based radicals. This is further facilitated by the small HFCs to vanadium.[21]

Full-molecule, broken-symmetry DFT calculations (B3LYP functional)[20] were also performed to augment the spectroscopic studies. The DFT-computed spin densities for $[(^{iPr}BPDI)V(NPh)_2]$ (Figure 5) and its chalcogenido analogs (Supporting Information, Figures S2–S4) establish that the unpaired spin is principally based on the bis(imino)pyridine chelate. The computed hyperfine values (Table 2) are in good agreement with the experimental parameters. Thus, the combined metrical, spectroscopic and computational data clearly establish that the electronic structures of $[(^{iPr}BPDI)V(E)_2]$ are best described as d^0 vanadium(V) compounds with a bis(imino)pyridine radical anion as the SOMO.

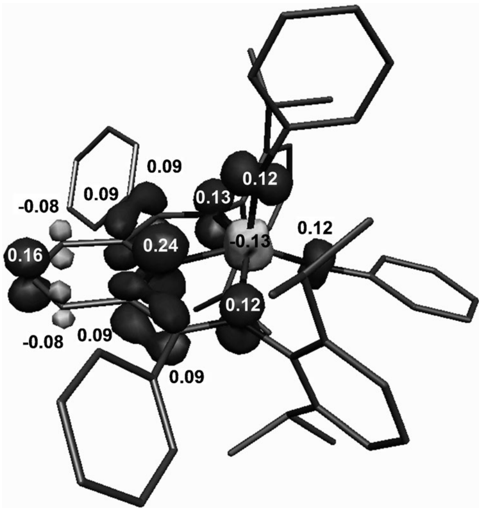
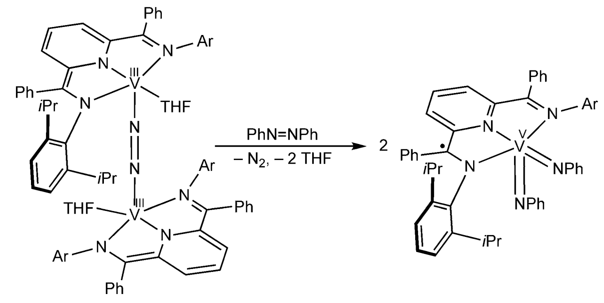


Figure 5. DFT-computed spin density plot for $[(^{iPr}BPDI)V(NPh)_2]$ obtained from Mulliken population analysis. Positive spin density is shown in dark and negative spin density is light.

Full-molecule DFT calculations (B3LYP functional) were also conducted on the hypothetical bis(imino)pyridine di(selenide), $[(^{iPr}BPDI)V(Se)_2]$. The Mulliken spin density plot for this molecule, reported in the Supporting Information, establishes considerable unpaired electron density on both the vanadium center and the selenido ligands in contrast to the observed monomeric $[(^{iPr}BPDI)V(E)_2]$. The electronic structure of this hypothetical molecule can be described as either $[(^{iPr}BPDI^{-})V^{III}(Se)_2]$ with two selenoxyl radicals, (Se$^{\bullet}$), or as $[(^{iPr}BPDI^{-})V^{IV}(Se)_2]$ with one terminal selinide and one selenoxyl radical (or a hybrid of all three). While it is unknown if $[(^{iPr}BPDI)V(Se)_2]$ forms initially from activation of gray selenium, the DFT calculations demonstrate that if formed, the compound would likely dimerize to yield the observed $[\{(^{iPr}BPDI)V(Se)\}_2(\mu_2\text{-}Se_2)]$. Broken-symmetry DFT calculations were also performed on a model complex of $[\{(^{iPr}BPDI)V(Se)\}_2(\mu_2\text{-}Se_2)]$, where the 2,6-diisopropylphenyl and backbone phenyl substituents were replaced with methyl groups. The results, presented in the Supporting Information, are consistent with two vanadium(IV), d^1 centers, each antiferromagnetically coupled to a $[BPDI]^{\bullet-}$ radical anion accounting for the observed diamagnetism. Additional antiferromagnetic coupling of the two metal centers through the $[\mu_2\text{-}Se_2]^{2-}$ ligand results in opposite signs of the spin density on the two vanadium ions in the broken-symmetry calculations.

Having established the electronic structures for $[(^{iPr}BPDI)V(E)_2]$, the course of electron flow and the role of the redox-active bis(imino)pyridine in azo N=N, O_2, S_8 and Se_n cleavage can be established (Scheme 1). Consistent with the previous report by Gambarotta and co-workers,[13] the starting $[\{(^{iPr}BPDI)V(THF)\}_2(\mu_2\text{-}N_2)]$ compound is best described as a vanadium(III) derivative with a two-electron reduced bis(imino)pyridine chelate and a bridging $[N_2]^{2-}$ ligand. As a hypothetical construct, considering the vanadium dinitrogen compound as a monomer, $[(^{iPr}BPDI)V(THF)N{=}]$, both the bis(imino)pyridine and the coordinated dinitrogen molecule each serve as one-electron reductants being oxidized to $[BPDI]^{\bullet-}$ and $[N_2]^0$, respectively. The other two electrons required for azo N=N or O_2 bond cleavage are vanadium-based as the metal is oxidized from V^{III} to V^{V}. Thus, small-molecule activation has been achieved where the reducing equivalents are a result of a cooperative effect between the supporting ligands and the metal center. The reactivity of the $[(^{iPr}BPDI)V(E)_2]$ compounds are currently under investigation in our laboratory with the goal of



$[\{(^{iPr}BPDI^{2-})V^{III}(THF)\}_2(\mu\text{-}N_2^{2-})]$ $[(^{iPr}BPDI^{-})V^{V}(NPh)_2]$

Scheme 1. Summary of metal–ligand cooperativity in azo N=N bond cleavage by reduced, redox-active bis(imino)pyridine vanadium compound.

exploiting metal–ligand cooperative redox chemistry in various group- and atom-transfer processes relevant to developing a synthetic Scheme for N_2 functionalization.

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[23] CCDC 859673 ($[\{(^{iPr}\mathrm{BPDI})\mathrm{V(THF)}\}_2(\mu_2\text{-}\mathrm{N}_2)]$), 859674 ($[(^{iPr}\mathrm{BPDI})\mathrm{V(NPh)}_2]$), 859676 ($[(^{iPr}\mathrm{BPDI})\mathrm{V(O)}_2]$), 859675 ($[(^{iPr}\mathrm{BPDI})\mathrm{V(S)}_2]$), and 859677 ($[\{(^{iPr}\mathrm{BPDI})\mathrm{V(Se)}\}_2(\mu_2\text{-}\mathrm{Se})]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.