Reduced Nitrogen Hydride Complexes of a Cofacial Metallodiporphyrin and Their Oxidative Interconversion. An Analysis of Ammonia Oxidation and Prospects for a Dinitrogen Electroreduction Catalyst Based on Cofacial Metallodiporphyrins

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Abstract: Oxidation of a bis(ammine) complex of a cofacial metallodiporphyrin, $(NH_3)_2Ru_2DPB$(1-*tert*-butyl-5-phenylimidazole)$_2$, leads to N–N bond formation and ultimately yields a bridged dinitrogen complex via bound hydrazine and diazene complexes. Each of the nitrogen hydrides involved in the successive two-electron/two-proton oxidative interconversions—the μ-diazene, μ-hydrazine, and bis(ammine) complexes—have been isolated and characterized. The electrochemical and acid–base properties of each of these complexes are reported. Mechanisms of ammonia oxidation are suggested. Stepwise two-electron/two-proton oxidations from the bis(ammine) complex to the hydrazine complex, from the hydrazine complex to the diazene complex, and from the diazene complex to the dinitrogen complex can be accomplished by *tert*-butyl hydroperoxide or sequential reaction of ferricinium hexafluorophosphate and a base. The prospects for electrocatalytic six-electron ammonia oxidation and electrocatalytic four-electron reduction of dinitrogen to hydrazine are discussed. On the basis of this analysis, reduction of hydrazine to ammonia by these systems is unlikely due to the energetically unfavorable thermolysis of the N–N bond of the bound hydrazine.

In the preceding paper[1] we described the preparation and characteristics of a dinitrogen complex of a diruthenium cofacial diporphyrin $(\mu\text{-}N_2)Ru_2DPB(Im^*)_2$[2] and discussed the advantages of the cofacial diporphyrins with respect to developing a molecular electrode catalyst for the reduction of dinitrogen. In this paper we describe the oxidative interconversion of bound ammonia to the bridged dinitrogen complex via bridged hydrazine and diazene complexes.[3] Careful analysis of each step in the oxidative interconversion should lead to a greater understanding of the mechanism of dinitrogen reduction at binuclear complexes and may facilitate the development of a robust molecular electroreduction catalyst for dinitrogen.

The mechanisms by which synthetic and biological nitrogen reduction systems operate are of great interest because of the inert nature of dinitrogen. Although great srides have been made toward understanding this problem, many questions remain. The differences in reduction at mono- vs bimetallic sites are only beginning to be uncovered: Whether the active sites in nitrogenase enzymes involve one or more metals is still debatable. The reduction of dinitrogen at a single metal center has been widely studied and is fairly well understood mostly because of the large volume of work done on complexes with the general formula $M^0(\text{phosphine})_4(N_2)_2$ or $M^0(\text{diphosphine})_2(N_2)_2$ where M = Mo or W.[4] The mechanism of protonation of these dinitrogen complexes has been thoroughly discussed in the literature.[5-7] On the basis of the results of studies on these monomeric systems in conjunction with enzymological studies, mechanisms for the reduction of dinitrogen by nitrogenase enzymes have been proposed.[8]

In order to compare more thoroughly dinitrogen reduction at mono- vs binuclear sites more examples of reactive binuclear dinitrogen complexes are needed. Compared with monomeric systems, relatively little is known about the mechanism of dinitrogen reduction by binuclear complexes. What is known about the activation/protonation of bridged dinitrogen complexes has been recently reviewed.[5,9] Of the cases where bridging dinitrogen complexes have been protonated to yield hydrazine or ammonia, protonations of the Ta and Nb dithiocarbamate complexes developed by Henderson et al.[10] are the most thoroughly understood from a mechanistic point of view. When treated with excess acid these complexes yield hydrazine quantitatively. It is proposed on the basis of kinetic data that stepwise addition of three protons followed by dissociation of one metal center and a final protonation step yield hydrazine.[11] Although some intermediates have been detected spectrophotometrically, none of them have been isolated. Only recently have there been reports of well-characterized bridging dinitrogen complexes being protonated to yield ammonia:[12] Thus far the details of those reactions have not been elucidated.

One of the chief disadvantages of utilizing bridged dinitrogen complexes as electrode catalysts for dinitrogen reduction is that once dinitrogen is reduced the two metal centers either decompose or diffuse away from each other. Additionally, as stated by Henderson,[9] in protonation reactions at binuclear dinitrogen complexes the stage at which the binuclear unit breaks up is not certain. This uncertainty complicates mechanistic studies. Surely if a binuclear site is involved in nitrogenase dinitrogen reduction the two metals are held in position. As previously discussed[1] cofacial metallodiporphyrins can be used to circumvent both of these problems because their robust coordination environments resist decomposition and the two metal centers are tethered and thus kept close to one another. Bridging intermediates are held

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[1] The preceding paper in this issue.

[2] Abbreviations: DPB = diporphyrinatobiphenylene tetraanion, *Im = 1-*tert*-butyl-5-phenylimidazole; NHE = normal hydrogen electrode; and $FeCp_2$ = ferrocene.

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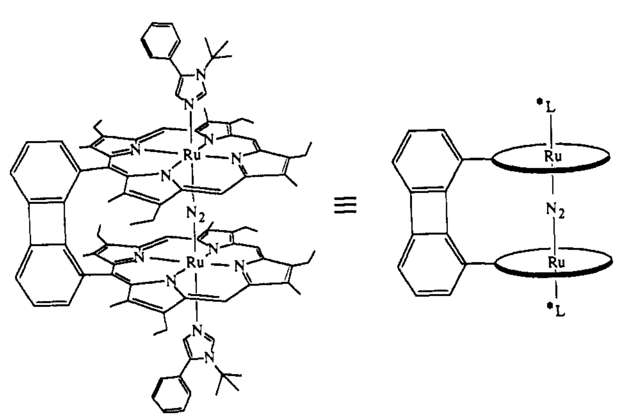

Figure 1. The bridged dinitrogen complex of the biphenylene cofacial diporphyrin $(\mu\text{-}N_2)Ru_2(^*L)_2DPB$.

in the cavity through chelation by the two metal centers.

In this paper we report details regarding the oxidative coupling of two ruthenium(II) ammine ligands to form a bridged dinitrogen complex of a cofacial metallodiporphyrin. In this system conversion from two ammines to the bridged dinitrogen complex proceeds through bridged hydrazine and diazene complexes rather the high-valent nitrido intermediates proposed in other systems.[13,14] We have isolated and characterized each of the intermediates involved and determined electrochemical and acid–base characteristics of each of the two-electron/two-proton conversions reported. Because these interconversions are the reverse of dinitrogen reduction, the results are discussed in the context of developing a dinitrogen electroreduction catalyst based upon cofacial metallodiporphyrins.

Results

Preparation of Compounds. The synthesis of the bridged dinitrogen complex $(\mu\text{-}N_2)Ru_2DPB(^*Im)_2$ (**2**) (Figure 1, *Im = 1-*tert*-butyl-5-phenylimidazole) and the replacement of the bound dinitrogen by Lewis bases have been described in the preceding paper.[1] Because the dinitrogen ligand may be replaced without replacement of the outside imidazoles, the dinitrogen complex is a useful synthon for the preparation of other complexes of the type $(L)_{inside}Ru_2DPB(^*Im)_2$. Direct synthesis of complexes by addition of the desired "inside" ligand to the bis(five-coordinate) complex, $Ru_2DPB(^*Im)_2$, is complicated by slow disproportionation of $Ru_2DPB(^*Im)_2$ to form a mixture of the metal–metal bonded dimer, Ru_2DPB, and $Ru_2DPB(^*Im)_4$. Coordinated dinitrogen acts as a protecting group for the two inner coordination sites.

We have taken advantage of the ligand substitution properties of the dinitrogen complex in preparing the bis(ammine) complex $(NH_3)_2Ru_2DPB(^*Im)_2$ (**3**) and the bridged hydrazine complex $(\mu\text{-}N_2H_4)Ru_2DPB(^*Im)_2$ (**4**). Treatment of dinitrogen complex **2** with an excess of either ammonia or hydrazine at ambient temperature in toluene yields the corresponding complexes quantitatively (Figure 2). In both cases the ^1H NMR spectrum indicates that the symmetry of the parent dinitrogen complex is preserved in the products. In addition, each of these complexes displays a high-field singlet (−8.75 ppm for $(NH_3)_2Ru_2DPB(^*Im)_2$ and −10.15 ppm for $(\mu\text{-}N_2H_4)Ru_2DPB(^*Im)_2$) that is assigned as the bound ammine or hydrazine resonance. These two peaks integrate to six and four protons per diporphyrin complex, respectively. The ring currents of both porphyrin rings cause the large upfield shifts of the internal axial ligand protons. The upfield shift of the hydrazine ligand in $(\mu\text{-}N_2H_4)Ru_2DPB(^*Im)_2$ is similar to that found in the previously reported, analogous complex $(\mu\text{-}N_2H_4)Ru_2DPB(PPh_3)_2$.[15]

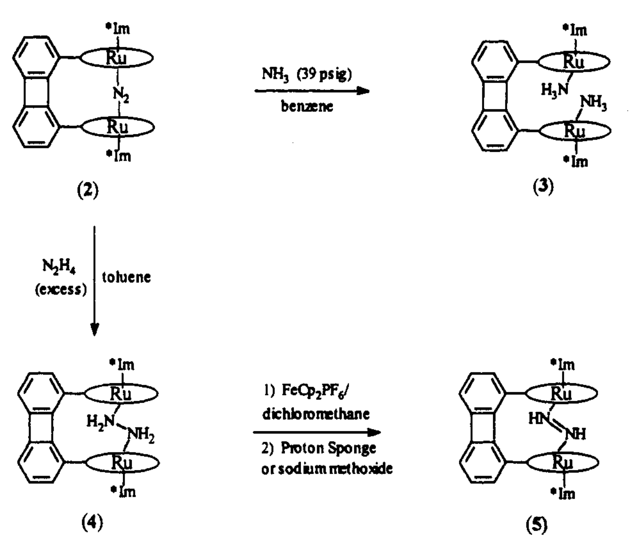

Figure 2. Synthesis of the bis(ammine) complex $(NH_3)_2Ru_2(^*L)_2DPB$, the μ-hydrazine complex $(\mu\text{-}N_2H_4)Ru_2(^*L)_2DPB$, and the μ-diazene complex $(\mu\text{-}N_2H_2)Ru_2(^*L)_2DPB$ from the dinitrogen complex.

The mass spectral data confirm the composition of the bis(ammine) and hydrazine complexes. In the mass spectrum, **3** displays a cluster corresponding to the molecular ion less one ammonia and **4** gives the expected molecular ion. Satisfactory elemental analyses have been obtained for **4**.

The preparation of diazene complex **5** required oxidation of the bridging hydrazine complex; this proved challenging because over-oxidation is a problem. We tried several oxidants[16] before finding that *tert*-butyl hydroperoxide was a suitable oxidant. Difficulties in controlling the extent of oxidation of **4** using *tert*-butyl hydroperoxide led us to explore the electrochemistry of this μ-hydrazine complex (vide infra). The electrochemical studies ultimately led to an even cleaner synthesis of **5**.

μ-Diazene complex **5** was prepared from **4** either by chemical oxidation with a stoichiometric amount of *tert*-butyl hydroperoxide in toluene or by stoichiometric electron-transfer oxidation with ferricinium hexafluorophosphate followed by deprotonation with a stoichiometric amount of Proton Sponge (Figure 2). In both cases the product is contaminated with a small amount of the dinitrogen complex; however, the latter procedure gives more reproducible results. After removal of the ferrocene and protonated Proton Sponge (by filtration through a short plug of silica gel) and removal of the solvent, the diazene complex is obtained in 90–95% purity, and the balance is the previously characterized dinitrogen complex **2**. Column chromatography failed to separate these two complexes.

Characterization of **5** as a μ-diazene complex is based on a number of lines of evidence. There are literature precedents[16] for stoichiometric oxidation of metallohydrazine complexes to metallodiazene complexes. Complex **5** is produced in high yield (>80%) from the well-characterized hydrazine complex **4** by two *independent* reaction pathways. More specifically, stepwise oxidation of **4** by $[FeCp_2^+][PF_6]$ yields a stable, bridged $Ru^{III}Ru^{III}$ hydrazine complex $\mathbf{4}^{2+}$ (vide infra) that when deprotonated by 2 equiv of base yields a compound that displays a proton NMR spectrum where both porphyrin rings are equivalent and both axial imidazoles remain bound to the complex. Additionally, the isolable complex **5** is oxidized to the well-characterized bridged dinitrogen complex **2** by *tert*-butyl hydroperoxide, another reaction for which there is considerable precedent. Although we have not been able to assign unambiguously the NH resonance in the proton NMR or definitively identify a band in the IR corresponding to a bound diazene absorption. We have observed the molecular ion cluster in the mass spectrum. We find the available spectroscopic data

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Table I. Redox Properties of the Bis(ammine), μ-Hydrazine, μ-Diazene, and μ-Dinitrogen Complexes in Dichloromethane (0.2 M Tetra-*n*-butylammonium Hexafluorophosphate) vs NHE[a]

	Bis(ammine) Complex		
$E_{1/2} = -0.19$ V	$n = 1$	$\Delta E_p = 74$ mV	II/II ↔ II/III
$E_{1/2} = -0.01$ V	$n = 1$	$\Delta E_p = 78$ mV	II/III ↔ III/III
$E_{1/2} = +1.13$ V	$n = 2$	$\Delta E_p = 77$ mV	ring oxidation
$E_{1/2} = +1.61$ V	$n = 2$	$\Delta E_p = 141$ mV	ring oxidation
	μ-Hydrazine Complex		
$E_{1/2} = -0.15$ V	$n = 1$	$\Delta E_p = 84$ mV	II/II ↔ II/III
$E_{1/2} = +0.14$ V	$n = 1$	$\Delta E_p = 87$ mV	II/III ↔ III/III
$E_{pa} = +1.34$ V	$n = 2$	na	ring oxidation
	μ-Diazene Complex		
$E_{1/2} = -0.22$ V	$n = 1$	$\Delta E_p = 70$ mV	II/II ↔ II/III
$E_{1/2} = +0.71$ V	$n = 1$	$\Delta E_p = 76$ mV	II/III ↔ III/III
$E_{1/2} = +1.34$ V	$n = 2$	na	ring oxidation
	μ-Dinitrogen Complex[9]		
$E_{1/2} = +0.03$ V	$n = 1$	$\Delta E_p = 65$ mV	II/II ↔ II/III
$E_{pa} = +0.73$ V	$n = 1$	na	II/III ↔ III/III

[a] $FeCp_2{}^{+/0} = 0.55$ V vs NHE.[18]

in conjunction with the reaction chemistry are compelling evidence for the proposed formulation. Observation of only one set of porphyrinic resonances in the proton NMR of **5** suggests that the two porphyrin rings are equivalent consistent with a μ-diazene complex. A monocoordinate diazene complex would make the two porphyrin rings inequivalent.

Solution Electrochemistry. The redox properties of the bis(ammine), μ-hydrazine, and μ-diazene complexes (in 0.2 M tetra-*n*-butylammonium hexafluorophosphate in dichloromethane) were studied by cyclic and rotating disk voltammetry. The results are summarized in Table I. A cyclic voltammogram for each complex is shown in Figure 3. $E_{1/2}$ values were determined from the cyclic voltammograms and reported vs NHE (see Experimental Section).

All observed redox couples of the described complexes were oxidations as verified by rotating disk voltammetry. No reduction waves were observable within the reduction potential limit of the solvent.[17] The first and second oxidations were assigned as metal-centered oxidations by comparing the potentials and the number of electrons transferred with these properties previously measured for other diruthenium DPB complexes.[15] The potentials and peak-to-peak separations of individual waves as well as the number of porphyrin ring-based oxidations observed vary considerably between the complexes; these data are shown in Table I. Although electrochemical solutions of the bis(ammine) and μ-hydrazine complexes were stable for long periods, the cyclic voltammograms of the diazene complex in dichloromethane/tetra-*n*-butylammonium hexafluorophosphate solution were only stable for about 15–30 min before other waves started appearing in the voltammograms.

In each complex studied, the first oxidation occurred between −0.15 and −0.25 V vs NHE. The position of the next oxidation wave depends on the degree of interaction between the metal centers. The difference in potential between the first oxidation and the second oxidation gives a rough measure of this interaction: bis(ammine), 190 mV; μ-hydrazine, 290 mV; μ-diazene, 930 mV.

The reversibility of the $Ru_2{}^{II/III}/Ru_2{}^{III/III}$ couple is especially important in the context of trying to prepare the bis(ammine) and μ-hydrazine complex dications, 3^{2+} and 4^{2+}. If this couple is reversible, then the $Ru_2{}^{III/III}$ complex should be stable enough to prepare chemically. We have found that this couple is reversible for each of the compounds reported except the dinitrogen complex.

Chemical Oxidations of Compounds and Deprotonation of Compounds. Oxidation of the bis(ammine) complex **3** leads to formation of a mixture of **4**, **5**, and **2** and can be accomplished either with an atom-transfer reagent, *tert*-butyl hydroperoxide for example, or by a step-wise reaction with an outer-sphere oxidant and a base, e.g., ferricinium hexafluorophosphate followed by sodium methoxide. Conditions have not yet been found for the quantitative transformation of **3** to **4**.

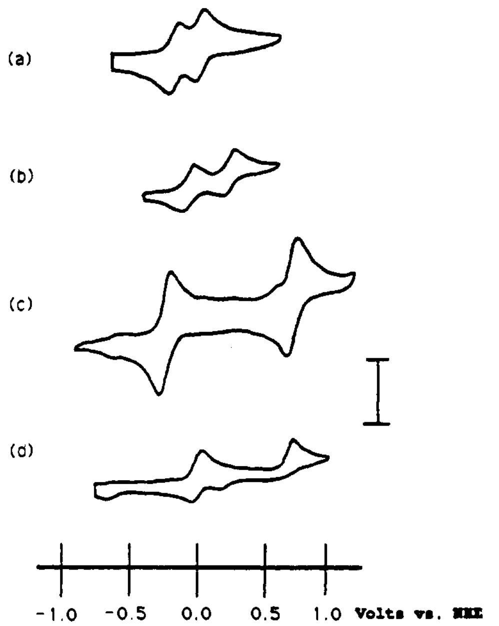

Figure 3. Cyclic voltammograms of (a) the bis(ammine) complex, (b) the μ-hydrazine complex, (c) the μ-diazene complex, and (d) the μ-dinitrogen complex. Conditions: Pt working electrode, 0.2 M $TBAPF_6$/dichloromethane, potential vs NHE. *Y* scale bar = 5 μamps for (c) and 10 μamps for the others.

Oxidation of **3** with 1 equiv of *tert*-butyl hydroperoxide resulted in a mixture containing 73% bis(ammine) complex, 17% μ-hydrazine complex, 6% μ-diazene complex, and 4% μ-dinitrogen complex (all determined by ^1H NMR). The products observed account for only 41% of the oxidizing equivalents added[18] (by ^1H NMR: assuming that all products are diamagnetic). This discrepancy could be the result of side reactions resulting in paramagnetic products which were not detected by ^1H NMR or of a bad titer on the *tert*-butyl hydroperoxide. Over-oxidation could be the result of indiscriminate oxidation by *tert*-butyl hydroperoxide.

Because oxidation with *tert*-butyl hydroperoxide was problematic, we examined a combination of outer-sphere oxidant and a base. Treatment of **3** with 2 equiv of ferricinium hexafluorophosphate produces a compound which gives a contact-shifted ^1H NMR spectrum, consistent with a $Ru^{III}Ru^{III}$ complex. When a benzene solution of this complex is stirred over sodium methoxide overnight, a mixture of bis(ammine) complex (72%), μ-hydrazine complex (9%), μ-diazene complex (16%), and μ-dinitrogen complex (4%) was formed. As observed by ^1H NMR, the components of this mixture only account for 53% of the oxidizing equivalents added[18] to the starting material (assuming that all products are diamagnetic). Attempts to deprotonate the dicationic bis(ammine) complex with Proton Sponge (a weaker, soluble base) failed even over long reaction times.

Oxidation of **3** by only 1 equiv of ferricinium hexafluorophosphate yields a paramagnetic complex which when stirred over solid sodium methoxide yields *no* bis(ammine) complex, *no* μ-hydrazine complex, and a trace of μ-dinitrogen complex (apparently the signals due to the primary reaction product(s) do not show up in the ^1H NMR or are broad enough to hinder their detection).

The complicated behavior seen in the oxidation of **3** is not observed for the μ-hydrazine complex **4**. Although over- and

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[17] (a) Electrochemical experiments in a solvent with a more negative potential limit, *o*-difluorobenzene[17b] for example, are in progress. (b) O'Toole, T. R.; Younathan, J. N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 3923–3926.

[18] The percentage of the oxidizing equivalents consumed in the reaction was calculated by (1) assuming that all products are diamagnetic, (2) adding up the number of equivalents of oxidant needed to obtain the products, and (3) comparing this value to the amount of oxidant actually added.

under-oxidation of **4** is observed with *tert*-butyl hydroperoxide, the yield of the desired diazene complex **5** is relatively high. Again the titer of the oxidant was problematic and oxidant was generally added until all **4** had been consumed (as determined by ^1H NMR). This technique results in a μ-diazene complex that is contaminated with 15–20% of the μ-dinitrogen complex **2**.

Oxidation of **4** by ferricinium hexafluorophosphate yields a product which gives a broadened, contact-shifted ^1H NMR spectrum. This type of ^1H NMR spectrum is consistent with formation of the dication $[(\mu\text{-}N_2H_4)Ru_2^{III/III}DPB(^*Im)_2]^{2+}$ ($\mathbf{4}^{2+}$). Deprotonation of $\mathbf{4}^{2+}$ can be accomplished with either sodium methoxide or Proton Sponge. The deprotonation by excess solid sodium methoxide is rapid: the reaction is complete within 20 min. Deprotonation with a stoichiometric quantity of Proton Sponge is surprisingly slower (the reaction can take up to 5 h). The rates of these deprotonations are anomalously slow; perhaps these result from conformational changes. In both cases, **5** is produced in greater than 90% yield. In each case the contaminant is mostly **2**: occasionally a trace of unreacted **4** is observed.

Oxidation of **5** using 2 equiv of *tert*-butyl hydroperoxide is rapid and yields the dinitrogen complex as the only diamagnetic complex. Oxidation by an outer-sphere oxidant would require an oxidant more powerful than $FeCp_2{}^+PF_6{}^-$ based on the redox couple measured in the cyclic voltammetric experiment. Preliminary attempts to oxidize the diazene complex cleanly with a more potent oxidant such as 1,1′-diacetylferricinium hexafluorophosphate[19] have been unsuccessful.

Efforts to deprotonate either **3** or **4** *before oxidation* with either sodium methoxide or Proton Sponge were unsuccessful.

Protonations of Complexes. Stirring a benzene solution of **3** with 2 equiv of trifluoroacetic acid for 30 min under a dinitrogen atmosphere yields the dinitrogen complex and the ammonium ion (eq 1).[20] Under acidic conditions (two equivalents of trifluoroacetic acid in benzene) the μ-hydrazine complex **4** reacts slowly (over the course of a week) and surprisingly yields a mixture consisting primarily of the μ-diazene **5** complex along with small amounts of **4** and **2** (eq 2). The nature of this slow reaction is not at all understood.

$$\underset{\mathbf{3}}{[Ru^{II}(NH_3)(NH_3)Ru^{II}]^0} \xrightarrow{CF_3CO_2H,\ N_2} \underset{\mathbf{2}}{[Ru^{II}(N{\equiv}N)Ru^{II}]^0} + 2NH_4^+ \quad (1)$$

$$\underset{\mathbf{4}}{[Ru^{II}(NH_2{-}NH_2)Ru^{II}]^0} \xrightarrow{CF_3CO_2H,\ N_2} \underset{\mathbf{5}}{[Ru^{II}(NH{=}NH)Ru^{II}]^0} \quad (2)$$

Discussion

One of the stated goals of these studies is to gain a better understanding of dinitrogen reduction at binuclear sites by studying the reverse reaction. This aim is not a new idea. Both Taube[14] and Sellmann[21] have reported oxidative N–N bond-forming reactions of transition metal ammine complexes and discussed their findings in the context of relating ammine oxidation to dinitrogen reduction. The oxidation of our bridged bis(ammine) complex to the dinitrogen complex via bound hydrazine and diazene complexes contrasts with oxidations of monomeric ruthenium(II) or osmium(II) ammine complexes. The monomeric complexes form bridged dinitrogen complexes through coupling of two nitrides that result from deprotonation of high-valent ruthenium[13] or osmium[14] fragments. Although the N–N bond formation observed in Sellmann's $Mn(Cp)(CO)_2L$ complexes presumably results from $2e^-/2H^+$ steps similar to those that we report here, the intermediate complexes involved are not stable and thus the details of electron and proton removal are not easily elucidated.

In this paper, bridged complexes involving two ruthenium centers have been characterized for dinitrogen, diazene, hydrazine, and two ammines. A cycle of two-electron changes interconverting these intermediates describes ammonia oxidation or its reverse, nitrogen reduction. The entire cycle represents an overall six-electron change. These stages have been connected by redox or ligand replacement reactions. In the redox processes, the sequence of electron–proton transfer is known; reversible cyclic voltammograms reveal the reduction potentials connecting members of this series. Approximate pK_a values have been determined for several cationic species in the cycle.

We now show that these data provide insight into the problem of generating a molecular electrode catalyst for the six-electron oxidation of two ammines to dinitrogen. Consideration of the reverse reaction sequence shows that it should be possible to reduce dinitrogen to hydrazine, a four-electron process. From this analysis, one can also understand the nature of the barrier which prevents further reduction of hydrazine to two ammines.

Retro Nitrogen Fixation. We have carried out a sequence of individual two-electron oxidations which convert two coordinated ammines into a bridged dinitrogen complex. The cycle has been closed by the replacement of dinitrogen by ammines. Together these reactions constitute the reverse reaction sequence of six-electron nitrogen fixation. We next consider each stage within a hypothetical catalytic oxidation cycle.

The bis(ammine) complex **3** is reversibly oxidized to the dicationic diruthenium(III) bis(ammine) complex $\mathbf{3}^{2+}$, a stable dication (eq 3). Because $\mathbf{3}^{2+}$ is stable until the addition of base, there must be an intermediate stage prior to the formation of an N–N bond from a pair of putative adjacent, neutral ruthenium(III) amides (eq 4). The latter have not been characterized. The electrochemical reversible potentials are known (Table I) and a pK_a value of ≅16 can be estimated for the base required for the deprotonation. The two bases employed in this study will not deprotonate the neutral bis(ammine) complex **3**.

$$\underset{\mathbf{3}}{[Ru^{II}(NH_3)(NH_3)Ru^{II}]^0} \overset{2e^-}{\rightleftharpoons} \underset{\mathbf{3}^{2+}}{[Ru^{III}(NH_3)(NH_3)Ru^{III}]^{2+}} \quad (3)$$

$$\underset{\mathbf{3}^{2+}}{[Ru^{III}(NH_3)(NH_3)Ru^{III}]^{2+}} \xrightarrow{-2H^+} [Ru^{III}(NH_2)(NH_2)Ru^{III}]^0 \rightarrow \underset{\mathbf{4}}{[Ru^{II}(NH_2\text{-}NH_2)Ru^{II}]^0} \quad (4)$$

It is somewhat surprising that both atom transfer oxidation (by *tert*-butyl hydroperoxide) and a step-wise outersphere electron-transfer oxidation (with $[FeCp_2][PF_6]$) followed by deprotonation (by sodium methoxide or Proton Sponge) give quite similar results in reactions with **3**. The mechanism(s) of coupling the two ammines in **3** is certainly complex. Due to the diversity of products formed upon deprotonation, any proposed reaction pathways must account for (1) a large portion of the dicationic bis(ammine) complex being converted back to the neutral bis(ammine) complex, (2) some of the material being oxidized past the hydrazine complex on to diazene and dinitrogen complexes, and (3) incomplete conversion of oxidizing equivalents to detectable products.

As stated above, $\mathbf{3}^{2+}$ is unreactive prior to addition of base. Once base is added, a number of possible pathways could lead to the observed products. The simplest mechanism is the one already presented (eqs 3 and 4); however, this reaction sequence alone does not explain the diverse product distribution or the missing oxidizing equivalents observed in these oxidations.

One way to explain the diverse product distribution is to consider that $[(NH_3)_2Ru_2^{III/III}DPB(^*Im)_2]^{2+}$ ($\mathbf{3}^{2+}$, $E_{1/2} = -0.01$ V) would oxidize the initial product $(\mu\text{-}N_2H_4)Ru_2^{II/II}DPB(^*Im)_2$ (**4**, $E_{1/2} = -0.15$ V) up to its monocation $(\mu\text{-}N_2H_4)Ru_2^{II/III}DPB(^*Im)_2^+$ ($\mathbf{4}^+$). This reaction would also form the half-oxidized ammine

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[19] 1,1′-Diacetylferricinium PF_6 is 530 mV more oxidizing than ferricinium PF_6. Wrighton, M. S.; Schneemeyer, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 6964–6971.

[20] (a) The dinitrogen complex was observed by proton NMR to be the major (>90%) porphyrinic product. Ammonia was analyzed following the procedure of Weatherburn[20b] and 150% of the theoretical amount was observed. The unrealistically high value is likely due to an error in the titer of the bis(ammine) complex stock solution used. (b) Weatherburn, M. W. *Anal. Chem.* **1967**, *39*, 971–974.

[21] Würminghausen, T.; Sellmann, D. *J. Organomet. Chem.* **1980**, *199*, 77–85.

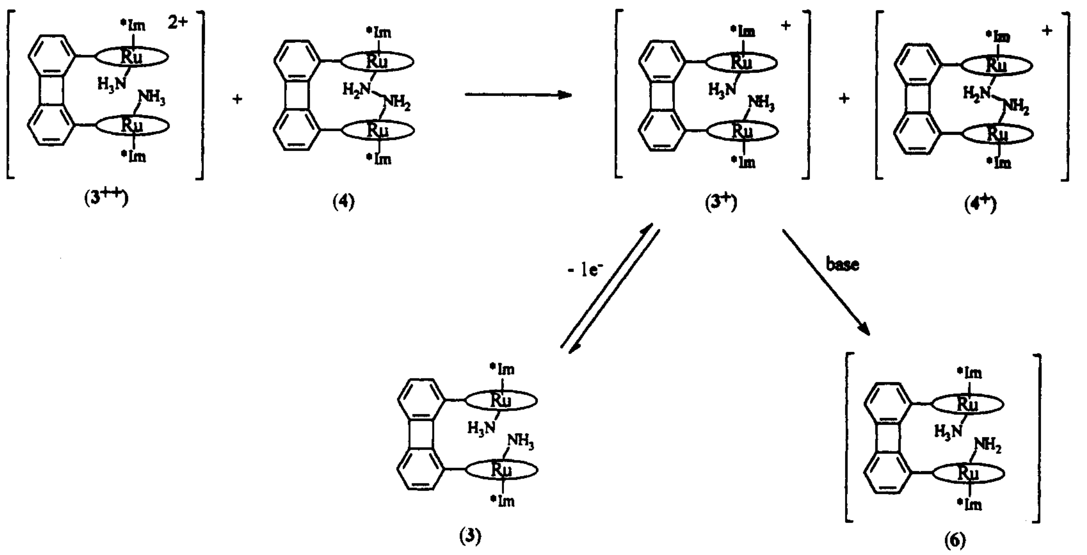

Figure 4. Reactions possibly involved in the oxidation of the bis(ammine) complex. "Base" refers to either Proton Sponge or sodium methoxide.

complex 3^+ (Figure 4). The two mixed-valent complexes 3^+ and 4^+ could each be deprotonated to give a neutral species such as **6**. For example, deprotonation of 3^+ would form **6**. We tried to prepare **6** independently but we found that oxidation of **3** by one electron followed by stirring over sodium methoxide yields no diamagnetic products. If this disproportionation mechanism is operative, production of **6**, which should be paramagnetic, could account for some of the missing oxidizing equivalents.

Although we have not tried to prepare the singly oxidized hydrazine complex 4^+ independently, it is possible that upon deprotonation it would yield another paramagnetic product (once again contributing to an apparent loss of oxidizing equivalents as well as producing over-oxidized products).

An alternative mechanism for oxidation of Ru(ammine) complexes which has precedent in monomeric systems such as $[Ru(NH_3)_5(pyr)]^{2+}$ and $[Ru(Bipy)(Trpy)(NH_3)]^{2+}$ involves base-promoted disproportionation between the two Ru^{III}(ammine) centers.[13] If this type of mechanism were operative, disproportionation and loss of two protons would lead to a cofacial diporphyrin containing one Ru^{II}(ammine) center and a Ru^{IV}imido center. We have no evidence for the existence of such a species nor have we observed products that implicate it in the reaction mixture.

Our reliance on ^{1}H NMR for analysis is the probable explanation for the apparently flawed material balance in the conversion of oxidizing equivalents (*tert*-butyl hydroperoxide) into products in the oxidation of **3**. Several ^{1}H NMR invisible paramagnetic products are probably formed. This proposal is supported by an experiment that shows that the deprotonation product of the monocationic complex 3^+ exhibits a very broad ^{1}H NMR spectrum.

The appearance of products oxidized beyond the μ-hydrazine complex probably results from rapid intermolecular electron-transfer steps occurring in competition with the slow N–N bond-forming reaction or the slow heterogeneous deprotonation using sodium methoxide. In either case, a slow step allows time for additional electron transfer chemistry to take place.

We cannot dismiss the possibility that several mechanisms exist for N–N bond formation in this system. We can however say that at least some of the bis(ammine) complex is oxidized through a mechanism involving bridged hydrazine and diazene complexes: a nitride coupling mechanism cannot explain the product distributions we have observed.

The N–N bond-forming step following proton transfer is unique in this cycle. It should not involve external electron transfer; it must be exothermic.[22] The microscopic reverse, bond cleavage, must then be endothermic and cannot be altered by changing the electrode potential. Such bond cleavage by this path cannot be driven by changing an electrode to strongly reducing potentials. Thus this thermal step should block the reduction of bound hydrazine to two ammines in nitrogen fixation in this symmetric coordination environment. Earlier[15] we reported a similar hydrazine complex $(\mu\text{-}N_2H_4)Ru_2DPB(PPh_3)_2$ is inert toward reduction. We will return to this point in a discussion of nitrogen fixation.

The next two-electron step is better understood. The μ-hydrazine complex **4** is reversibly oxidized to the stable dicationic μ-hydrazine complex 4^{2+} (eq 5). The weaker base, Proton Sponge, deprotonates 4^{2+} to a neutral, bridged diazene complex **5** (eq 5). Thus the order of the sequence of two-electron oxidation and then two-proton removal is established and the E^0 and pK_a values are known or can be estimated (Table I and eq 5).

$$\underset{\mathbf{4}}{[Ru^{II}(NH_2{-}NH_2)Ru^{II}]^0} \overset{-2e^-}{\rightleftharpoons} \underset{pK_a \cong 12}{[Ru^{III}(NH_2{-}NH_2)Ru^{III}]^{2+}} \xrightarrow{+2H^+} \underset{\mathbf{5}}{[Ru^{II}(NH{=}NH)Ru^{II}]^0} \qquad (5)$$

The final two-electron oxidation step (converting the bridged diazene complex to the bridged dinitrogen complex) involves the sequential, stepwise removal of two electrons followed by loss of two protons (eq 6). Reversible cyclic voltammetry has established

$$\underset{\mathbf{5}}{[Ru^{II}(NH{=}NH)Ru^{II}]^0} \overset{-2e}{\rightleftharpoons} \underset{\mathbf{5}^{2+}}{[Ru^{III}(NH{=}NH)Ru^{III}]^{2+}} \xrightarrow{+2H^+} \underset{\mathbf{2}}{[Ru^{II}(N{\equiv}N)Ru^{II}]^0} \qquad (6)$$

the E^0 values of the two reversible oxidations (Table I), but this reaction has not been achieved with outersphere chemical oxidants. As predicted by the electrochemistry, ferricinium ion does not have a sufficiently high potential to oxidize **5**. Oxidation by the more potent oxidant, 1,1′-diacetylferricinium hexafluorophosphate, has not been successful. Although we have not been able to measure the acidity of the diazene complex dication, it must have a low pK_a, a point we will return to when considering the reverse reaction. The atom-transfer oxidant, *tert*-butyl hydroperoxide, effects this transformation.

The final stage in a catalytic cycle of "retro nitrogen fixation" involves the displacement of dinitrogen by two ammines. We have performed this reaction in nonaqueous solution (benzene) and it is slow for the diruthenium(II) dinitrogen complex. Reversible one-electron electrochemical oxidation of the dinitrogen complex has been carried out; the singly oxidized product is much more labile but we have not yet studied the rates of its replacement by

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[22] Entropic changes should be small in this intramolecular reaction.

other ligands.[1] Under the limiting potential required for the overall catalytic cycle, the dinitrogen complex would be oxidized thus facilitating replacement of dinitrogen by ammonia.

Having in hand each two-electron, two-proton redox reaction, and the ammine/dinitrogen displacement reaction, it is instructive to consider the prospects for developing a fully electrocatalytic system. For an electrocatalytic oxidation cycle to function, it is clear that the electrode potential must be held at or near the highest (most oxidizing) potential necessary to effect the highest energy oxidation reaction within the catalytic cycle. In the present case that step is the second oxidation of the diazene complex, $E^0 = +0.71$ V vs NHE (Table I). Similarly the oxidation sequence requires a basic medium; the overall catalytic cycle must operate at or above the pH corresponding to the pK_a of the least acidic oxidized stage. This base must be chosen such that it is not oxidized at this potential. For the present case that corresponds to a p$K_a \cong 16$ for deprotonation of the dicationic diruthenium(III) bis(ammine) complex $\mathbf{3}^{2+}$, the least acidic complex in the cycle.

Although we have not yet achieved an electrocatalytic six-electron oxidation of two ammonia molecules, each step has been demonstrated individually, and we can gauge the minimum potential and pH for such a process to occur. Our initial attempts to catalyze this reaction utilized the dinitrogen complex imbibed upon edge-plane graphite. Unfortunately, a blank reaction using the bare, catalyst-free electrode showed a catalytic current in the presence of aqueous ammonium hydroxide. Future research in this area should be directed toward attaching these complexes to an inert electrode surface. Such adsorbed catalysts should be superior because the electron-transfer steps should be fast. All complexes and intermediate stages would then be held at this potential, possibly avoiding intermolecular disproportionation reactions which may occur in solution through electron transfer. Such reactions may account for the less than quantitative yields we have observed in the individual chemical oxidations.

The Prospect of Catalytic Nitrogen Fixation. Although the overall catalytic six-electron oxidation of two ammines to dinitrogen is intellectually interesting, it is more important to understand its reverse reaction, catalytic nitrogen reduction (fixation). This is especially true because of the long-standing, worldwide interest in enzymatic nitrogen reduction.

We begin this analysis by considering a seemingly intractable step, the first $2e^-/2H^+$ reduction of coordinated dinitrogen. It seems clear that for the reduction cycle protons should be added before electrons, which is the reverse of the oxidation cycle previously discussed. In the reduction cycle, an acidic medium would be required, whereas a basic medium was necessary for oxidation. However, the dinitrogen complex shows no apparent reaction with CF_3CO_2H;[1] preliminary experiments with reducing agents in acidic media have not afforded any well-characterized products. Nevertheless, this approach is promising, in light of the electrochemical results. Recall that according to cyclic voltammetry the bridging diazene complex undergoes a reversible overall two-electron oxidation. The putative dicationic diazene complex $\mathbf{5}^{2+}$ can lose two protons, forming the dinitrogen complex; it is probably a moderately strong acid. It is clear that a doubly protonated dinitrogen complex has the same stoichiometry, and undoubtedly the same structure as this dicationic diazene complex, eq 7. Because the cyclic voltammetric oxidation of the μ-diazene complex **5** is reversible, in an acidic medium the doubly protonated dinitrogen complex should then be reducible to the neutral diazene complex. We have not yet achieved this transformation. A further complication, the possibility of cis or trans stereoisomers of the diazene complex, has not been taken into account. We do not know which stereoisomers are involved. There might be different reactivities.

The reaction shown in eq 7 may also be complicated; if the

$$\underset{\mathbf{2}}{[\mathrm{Ru^{II}(N{\equiv}N)Ru^{II}}]^0} \xrightarrow{+2H^+} \underset{\mathbf{5}^{2+}}{[\mathrm{Ru^{III}(NH{=}NH)Ru^{III}}]^{2+}} \xrightarrow{+2e^-} \underset{\mathbf{5}}{[\mathrm{Ru^{II}(NH{=}NH)Ru^{II}}]^0} \quad (7)$$

reducing equivalents are not delivered rapidly, $\mathbf{5}^{2+}$ (which is a powerful oxidizing agent) could destroy part of the dinitrogen complex through intermolecular oxidation. For this reason, a catalyst adsorbed on the electrode could give cleaner reactions.

The next step, a two-electron/two-proton reduction of the diazene complex **5**, can be considered from a similar point of view. Reversible two-electron oxidation (in two one-electron steps) of the well-characterized bridging hydrazine complex **4** has been demonstrated by cyclic voltammetry. The doubly-oxidized dication is a weak acid since double deprotonation of this dicationic complex by Proton Sponge (p$K_a \cong 12$) affords the characterized diazene complex. The reverse protonation of the neutral diazene complex should thus be possible (eq 8). Thus *conceptually* through these

$$\underset{\mathbf{5}}{[\mathrm{Ru^{II}(NH{=}NH)Ru^{II}}]^0} \xrightarrow{+2H^+} \underset{\mathbf{4}^{2+}}{[\mathrm{Ru^{III}(NH_2{-}NH_2)Ru^{III}}]^{2+}} \xrightarrow{+2e^-} \underset{\mathbf{4}}{[\mathrm{Ru^{II}(NH_2{-}NH_2)Ru^{II}}]^0} \quad (8)$$

individual steps we have connected the dinitrogen complex with the diazene and the hydrazine complexes by stages, each involving double protonation followed by two-electron reduction. Taken together eqs 7 and 8 could lead to four-electron reduction of coordinated dinitrogen to hydrazine.

We have already demonstrated, from examining the reverse reaction, that electrochemical reduction of the diruthenium(II) hydrazine complex to the diruthenium(II) bis(ammine) complex is highly improbable at any reducing potential. This is due to an interesting thermal step; in the reduction cycle this would require a strongly endothermic reaction to rupture the N–N bond.

To consummate a catalytic cycle for the four-electron reduction of dinitrogen to hydrazine we must replace coordinated hydrazine with dinitrogen. Although the replacement of two ammines by dinitrogen does occur under acidic conditions, our preliminary attempts to carry out the similar hydrazine replacement have failed. One explanation is the bridging chelation of the hydrazine. We are presently studying this general problem. If this step could be resolved, a catalytic four-electron reduction of dinitrogen would be feasible.

From these studies, we find that if a catalytic four-electron dinitrogen reduction is to occur the electrode potential would need to be slightly more negative than −0.22 V vs NHE (the potential to reduce the diazene complex monocation). The acid needed to protonate the least basic site (presumably the dinitrogen ligand) would have to be at least as strong as trifluoroacetic acid, probably stronger than that. It is interesting to note that this potential and acidity are thermodynamically sufficient to reduce protons to dihydrogen; the stoichiometry of biological nitrogen fixation includes a two-electron reduction of protons to dihydrogen! Additionally we note that this cofacial system has another parallel with biological reduction because dihydrogen is replaced by dinitrogen at both nitrogenase active sites and our diruthenium complex.

What are the prospects for a six-electron reduction of dinitrogen to ammonia? It seems evident that such a reaction would require a different path. As discussed in the preceding paper in this issue, for bridging dinitrogen complexes having a total d-electron count of eight or less greatly reduces the N–N bond order, and correspondingly increases the M–N bond order.[1] The extreme is a pair of metal nitrides. This path would require earlier transition metals, such as molybdenum or vanadium, two metals that are present in certain nitrogenase enzymes.

Conclusion

Careful analysis of the redox properties, approximate pK_a values, and ligand replacement reactions of dinitrogen, diazene, hydrazine, and ammonia bound to a diruthenium cofacial diporphyrin shows that the overall six-electron oxidation of two ammines to dinitrogen and the overall four-electron reduction of dinitrogen to hydrazine should each be feasible. The required electrode potentials and pH ranges for these two electrochemical processes can be predicted from the present studies of individual steps. However, a catalytic cycle cannot be completed unless the hydrazine can be replaced by a dinitrogen. Our analysis also shows that an overall six-electron reduction to two ammines would fail with our present system because of a thermal bond breaking/making reaction in the catalytic cycle. This analysis represent a rare anatomy of a multielectron redox cycle and it may eventually offer insights into metal–enzyme catalyzed reactions.

Experimental Section

Materials. Tetra-*n*-butylammonium hexafluorophosphate was prepared as described in the preceding paper.[1] Ferricinium hexafluorophosphate was prepared following the literature procedure,[23] dried overnight under vacuum at ambient temperature, and immediately taken into the drybox. Hydrazine (Aldrich) was distilled from sodium hydroxide under argon. Silica gel for use in the drybox was evacuated and dried for 24 h at 1×10^{-2} Torr and 200 °C. Solvents for use in the drybox were distilled from blue or purple sodium benzophenone ketyl solutions (benzene, toluene, hexanes, and tetrahydrofuran), from $\mathrm{P_2O_5}$ (dichloromethane), and from $\mathrm{NaOCH_3}$ (methanol). Deuterated benzene (as an NMR solvent for air-sensitive complexes) was stirred over sodium benzophenone ketyl overnight and distilled off by vacuum vapor-phase transfer after degassing by five cycles of freeze–pump–thaw. All other reagents were used as received.

Physical Measurements. ^{1}H NMR spectra were recorded on either a Nicolet NT-300 or a Varian XL-400 Fourier transform spectrometer using benzene-d_6 as solvent and referenced to TMS. Electronic absorption spectra were measured on either an HP 8452A or a Cary 219 UV–visible spectrophotometer. Mass spectra were measured at the Mass Spectrometry Facility, University of California, San Francisco.

All electrochemical measurements were made in dichloromethane solutions with tetra-*n*-butylammonium hexafluorophosphate as backing electrolyte. A 2-mm platinum disk was used as the working electrode. A $\mathrm{Ag/AgNO_3}$ pseudoreference electrode was used and all potentials were measured versus the ferrocene/ferricinium couple by adding ferrocene at the end of each experiment. Potentials are reported vs NHE and were converted to this reference scale by using $E_{1/2}(\mathrm{FeCp_2}^{+/0}) = +0.55$ V vs NHE.[24] A special small-volume cell was used for all cyclic voltammetric and rotating disk electrochemical experiments.[25] A PAR 173 potentiostat/galvanostat, a PAR 175 universal programmer, and an HP 7046B X–Y recorder were used to make all electrochemical measurements.

Preparation of Compounds. The bis(five-coordinate) complex $\mathrm{Ru_2DPB(^*Im)_2}$ (**1**) and the bridged dinitrogen complex $(\mu\text{-}\mathrm{N_2})\mathrm{Ru_2DPB(^*Im)_2}$ (**2**) were prepared as previously described.[1]

$\mathbf{(NH_3)_2Ru_2DPB(^*Im)_2}$ (3). The dinitrogen complex $(\mu\text{-}\mathrm{N_2})\mathrm{Ru_2(^*Im)_2DPB}$ (19.0 mg in 5 mL of benzene) was stirred under 39 psi of ammonia for 19 h. Removal of the solvent under reduced pressure gave the bis(ammine) complex $\mathrm{(NH_3)_2Ru_2DPB(^*Im)_2}$ in quantitative yield.

^{1}H NMR ($\mathrm{C_6D_6}$, ppm): Porphyrinic resonances: $\mathrm{H_{meso}}$ 8.79 (s, 2 H), 8.38 (s, 4 H); biphenylene 7.01 (d, 2 H), 6.92 (t, 2 H), 6.79 (t, 2 H); $-\mathrm{C}H_2\mathrm{CH_3}$ 3.36 (m, 16 H); $-\mathrm{C}H_3$ 3.29 (s, 12 H), 2.71 (s, 12 H); $-\mathrm{CH_2C}H_3$ 1.55 (t, 12 H), 1.36 (t, 12 H). Imidazole resonances: *p*-phenyl 6.36 (t, 2 H); *m*-phenyl 6.15 (t, 4 H); *o*-phenyl 5.31 (d, 4 H); $\mathrm{H_{imidazole}}$ 1.65 (s, 2 H), 1.51 (s, 2 H); *tert*-butyl −0.49 (s, 18 H); $-\mathrm{NH_3}$ −8.75 (s, 6 H). UV/visible (toluene, nm (log ε)): 393 (5.33), 500 (4.33), 524 (4.69). Mass spectrum: LSIMS, tetraglyme, cluster, 1721, {$[\mathrm{M + H}]^+ - \mathrm{NH_3}$}. Clusters are also seen which correspond to (1) loss of one imidazole and one ammine ligand and (2) to loss of both imidazoles and both ammine ligands.

$\mathbf{(\mu\text{-}N_2H_4)Ru_2DPB(^*Im)_2}$ (4). The dinitrogen complex $(\mu\text{-}\mathrm{N_2})\mathrm{Ru_2DPB(^*Im)_2}$ (20.3 mg in 4 mL of toluene) was stirred with 1.0 mL of anhydrous hydrazine under a dinitrogen atmosphere for 24 h. The solvent was removed under reduced pressure to give the bridged hydrazine complex $(\mu\text{-}\mathrm{N_2H_4})\mathrm{Ru_2DPB(^*Im)_2}$ in quantitative yield. Recrystallization from methylene chloride/methanol produced analytically pure, brown microcrystals. Calculated for $\mathrm{C_{102}H_{112}N_{14}Ru_2}$: C, 70.56; H, 6.50; N, 11.30. Found: C, 70.92; H, 6.20; N, 11.18.

^{1}H NMR ($\mathrm{C_6D_6}$, ppm): Porphyrinic resonances: $\mathrm{H_{meso}}$ 8.53 (s, 6 H); biphenylene 7.03 (d, 2 H), 6.97 (d, 2 H), 6.82 (t, 2 H); $-\mathrm{C}H_2\mathrm{CH_3}$ 3.80 (m, 4 H), 3.63 (m, 4 H), 3.50 (m, 8 H); $-\mathrm{C}H_3$ 3.23 (s, 12 H), 3.00 (s, 12 H); $-\mathrm{CH_2C}H_3$ 1.68 (t, 12 H), 1.62 (t, 12 H). Imidazole resonances: *p*-phenyl 6.30 (t, 2 H); *m*-phenyl 6.08 (t, 4 H); *o*-phenyl 5.15 (d, 4 H); $\mathrm{H_{imidazole}}$ 1.40 (s, 2 H), other $\mathrm{H_{imidazole}}$ peak obscured by $-\mathrm{CH_2C}H_3$ resonances; *tert*-butyl −0.57 (s, 18 H); $-\mathrm{N_2H_4}$ −10.15 (s, 4 H). UV/visible (toluene, nm (log ε)): 387 (5.30), 500 (4.30), 522 (4.62). Mass spectrum: LSIMS (tetraglyme), 1736, $[\mathrm{M + H}]^+$, cluster. A cluster is also seen which corresponds to loss of one imidazole and loss of both imidazoles and hydrazine.

$\mathbf{(\mu\text{-}N_2H_2)Ru_2DPB(^*Im)_2}$ (5). (a) A toluene solution of *tert*-butyl hydroperoxide (2.1 mL of a 345 μM solution) was added dropwise to a solution of the hydrazine complex $(\mu\text{-}\mathrm{N_2H_4})\mathrm{Ru_2DPB(^*Im)_2}$ (1.2 mg in 2 mL of toluene). The solvent was removed under vacuum to give the product $(\mu\text{-}\mathrm{N_2H_2})\mathrm{Ru_2DPB(^*Im)_2}$ contaminated by a small amount of the dinitrogen complex.

(b) To a solution of $(\mu\text{-}\mathrm{N_2H_4})\mathrm{Ru_2DPB(^*Im)_2}$ (4.1 mg in 2 mL of toluene) was added 830 μL of a stock solution (8.7 mg in 5 mL of dichloromethane) of ferricinium hexafluorophosphate. The reaction mixture was stirred for 1 h before 395 μL of a stock solution (5.1 mg in 2 mL of toluene) of Proton Sponge was added. Stirring was continued for 3 h. The solvent was removed under reduced pressure and the residue taken up in hexanes. The resulting solution was loaded onto a 4-cm plug of silica gel in a disposable pipet (packed using hexanes). The column was washed with hexanes to elute the ferrocene. Elution with 30% toluene in hexanes eluted the product leaving the protonated Proton Sponge at the top of the column. Removal of the solvent from the eluent under vacuum yields the diazene complex.

^{1}H NMR ($\mathrm{C_6D_6}$, ppm): Porphyrinic resonances: $\mathrm{H_{meso}}$ 8.75 (s, 4 H), 8.66 (s, 2 H); biphenylene 7.15–6.65 (m, 6 H); $-\mathrm{C}H_2\mathrm{CH_3}$ 3.92 (m, 4 H), 3.71 (m, 4 H), 3.51 (m, 8 H); $-\mathrm{C}H_3$ 3.28 (s, 12 H), 3.03 (s, 12 H); $-\mathrm{CH_2C}H_3$ 1.70–1.60 (m, 24 H). Imidazole resonances: *p*-phenyl 6.29 (t, 2 H); *m*-phenyl 6.08 (t, 4 H); *o*-phenyl 5.13 (d, 4 H); $\mathrm{H_{imidazole}}$ 1.14 (s, 2 H), 1.04 (s, 2 H); *tert*-butyl −0.61 (s, 18 H). UV/visible (toluene, nm): 390 (Soret), 510, 534. Mass spectrum: LSIMS (tetraglyme), 1734, $[\mathrm{M + H}]^+$, cluster. A calculated molecular ion cluster based on $\mathrm{C_{102}H_{110}N_{14}Ru_2}$ closely matches the isotopic distribution of the observed cluster.

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