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**Authors**

Wright, Ashley M

Hayton, Trevor W

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# **Understanding the Role of Hyponitrite in Nitric Oxide Reduction**

Ashley M. Wright and Trevor W. Hayton\*

Department of Chemistry and Biochemistry, University of California Santa Barbara,

Santa Barbara CA 93106

Email: [hayton@chem.ucsb.edu](mailto:hayton@chem.ucsb.edu)

## **Abstract**

Herein, we review the preparation and coordination chemistry of the *cis* and *trans* isomers of hyponitrite,  $[\text{N}_2\text{O}_2]^{2-}$ . Hyponitrite is known to bind to metals via a variety of bonding modes. In fact, at least eight different bonding modes have been observed, which is remarkable for such a simple ligand. More importantly, it is apparent that the *cis* isomer of hyponitrite is more reactive than the *trans* isomer, as the barrier of  $\text{N}_2\text{O}$  elimination from *cis*-hyponitrite is lower than that of *trans*-hyponitrite. This observation may have important mechanistic implications for both heterogeneous  $\text{NO}_x$  reduction catalysts and *NO Reductase*. However, our understanding of the hyponitrite ligand has been limited by the lack of a general route to this fragment, and most instances of its formation have been serendipitous.

## 1. Introduction

Nitric oxide reduction plays a key step in the global nitrogen cycle. In biological systems, this reaction is performed by *NO reductase* (NOR) and *flavodiiron NO reductase* (FDP),<sup>1-12</sup> which convert two equivalents of nitric oxide, two reducing equivalents, and two protons, into N<sub>2</sub>O and water. The exact order of proton and electron additions during their catalytic cycles is not known, nor is the mechanism by which the N-N bond of N<sub>2</sub>O is formed.<sup>5,7</sup> As a result, there is much speculation and debate about how these enzymes operate;<sup>13-15</sup> however, a common intermediate to many of these mechanistic proposals is the hyponitrite moiety, [N<sub>2</sub>O<sub>2</sub>]<sup>2-</sup>,<sup>1,7,16</sup> which is formed via coupling of two nitric oxide molecules.

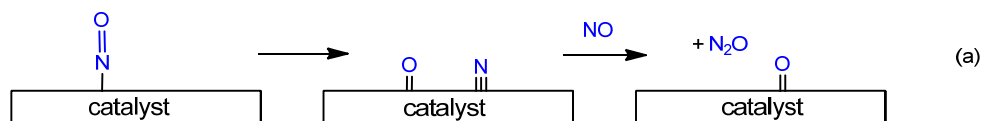
Nitric oxide reduction is also necessary for controlling NO<sub>x</sub> emissions in automotive exhaust. In modern vehicles, this is done using a “three way” catalytic converter.<sup>17,18</sup> The current catalysts work exceptionally well;<sup>18</sup> however, they utilize precious metals (e.g., Pt and Rh), and there is considerable interest in replacing these expensive noble metals with cheaper, earth abundant elements.<sup>18-20</sup> In addition, due to tightening regulatory requirements there is concern that current catalyst systems will not be able to meet future NO<sub>x</sub> emission standards, both in Europe and North America.<sup>18</sup> Even before these challenges were recognized, though, there had been considerable interest in understanding the mechanism of heterogeneous NO reduction in catalytic converters.<sup>20-25</sup> Many research groups have examined this reaction, and the generally accepted mechanism is thought to involve initial NO dissociation to form surface bound nitride and oxide (Scheme 1a).<sup>18,24-31</sup> However, more recent experimental work suggests an

alternate mechanism could also be operative. In this pathway, NO reduction proceeds via a “hyponitrite-like”  $(\text{NO})_2$  dimer (Scheme 1b),<sup>20,22,32-34</sup> and, in fact, this intermediate has been detected directly with IR spectroscopy on Ag(111) at low temperatures (70 K).<sup>22,35</sup>  $(\text{NO})_2$  dimers have also been imaged on Cu(110) using scanning tunneling microscopy (STM),<sup>33</sup> and more recently, evidence for the formation  $(\text{NO})_3$  trimers on Cu(111) at 6 K has been collected with STM.<sup>36</sup> Nitric oxide also forms dimers on Pd(111) under certain conditions, as revealed by *in situ* infrared reflection absorption spectroscopy (IRAS).<sup>37</sup>

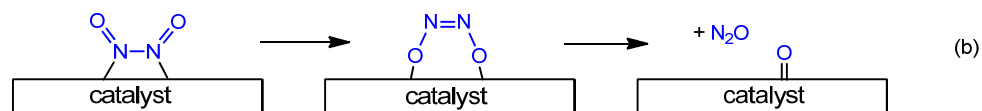
Calculations performed on several different catalyst systems also support the intermediacy of an  $(\text{NO})_2$  dimer during nitric oxide reduction. For example, DFT calculations on the reduction of NO by Ag on alumina supports the  $(\text{NO})_2$  dimer mechanism.<sup>20,38,39</sup> Similarly, calculations suggest that NO reduction on Au can occur via an  $(\text{NO})_2$  intermediate. Moreover, this pathway of NO reduction is thought to be dominant at low temperatures.<sup>40</sup> NO reduction catalyzed by Pd(111) also occurs via a hyponitrite intermediate.<sup>41</sup>

**Scheme 1.** Two Proposed Routes of  $\text{NO}_x$  Reduction on Metal Surfaces

**Traditional mechanism:**



**Hyponitrite mechanism:**



Given the uncertainty surrounding the mechanisms of NO reduction in heterogeneous catalysis, as well as in biological systems, it is clear that further study in this area is

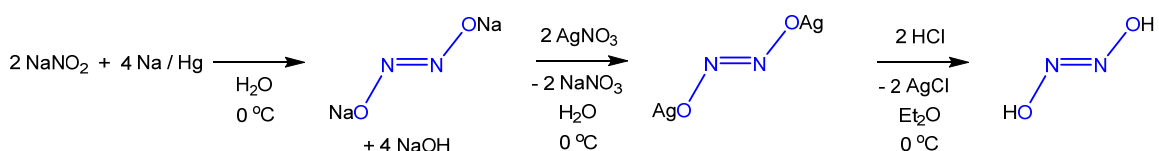
warranted. Of particular relevance to this Forum Article is the proposed intermediacy of the hyponitrite moiety,  $[\text{N}_2\text{O}_2]^{2-}$ , during the reduction of nitric oxide. This moiety is known to bind to metal ions to form discrete, well-defined coordination complexes,<sup>42</sup> suggesting a role for homogenous model systems in the efforts to evaluate the proposed mechanisms of  $\text{NO}_x$  reduction. However, the hyponitrite ligand is poorly understood, in part, because there is not yet a rational, broadly applicable method for generating and ligating this moiety to a transition metal ion. In this regard, this Forum Article will review the fundamental properties of the hyponitrite ion, describe its ligation to metal ions, and review its reactivity, in an effort to spur further development in this area.

## 2. Overview of Hyponitrite Chemistry

**2.1. *cis*- and *trans*-hyponitrous acid and its salts.** To better understand the reactivity of the metal-bound hyponitrite moiety, it is informative to review the chemistry of the parent molecule, hyponitrous acid ( $\text{HONNOH}$ ), along with its salts. Anhydrous hyponitrous acid can be prepared in a multi-step procedure from sodium nitrite. First,  $\text{NaNO}_2$  is reduced with Na / Hg amalgam in water at 0 °C to generate sodium *trans*-hyponitrite (Scheme 2).<sup>43-45</sup> Sodium *trans*-hyponitrite is then reacted with an aqueous solution of  $\text{AgNO}_3$ , which results in precipitation of silver hyponitrite,  $\text{Ag}_2\text{N}_2\text{O}_2$ . Subsequent reaction of silver hyponitrite with anhydrous HCl in  $\text{Et}_2\text{O}$  results in the formation of *trans*- $\text{H}_2\text{N}_2\text{O}_2$  (Scheme 2),<sup>45</sup> which can be isolated as a white crystalline solid. Great care must be taken in handling solid hyponitrous acid as it is reportedly explosive. Also note that the yield for the first step of this sequence is reportedly quite low (20%) and the isolated product is often impure.<sup>46</sup> Interestingly, *trans*-hyponitrous

acid was only recently characterized by X-ray crystallography.<sup>45</sup> It was found to co-crystallize within the salt,  $[\text{HEt}_2\text{NCH}_2\text{CH}_2\text{NEt}_2\text{H}][\text{HN}_2\text{O}_2]\cdot\text{H}_2\text{N}_2\text{O}_2$ .<sup>45</sup> In the solid state, *trans*-hyponitrous acid features an N=N bond length of 1.226(4) Å, N-O bond lengths of 1.363(3) Å, and an N-N-O angle of 109.9(3)°. <sup>45</sup> These parameters are similar to those featured by *trans*-hyponitrite (see below), and are consistent with the resonance structure shown in Scheme 2.

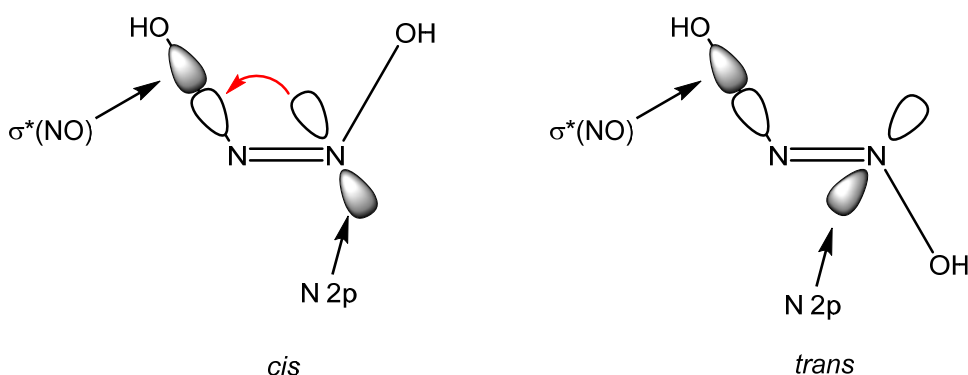
**Scheme 2.** Synthesis of *trans*-hyponitrous acid.



When prepared according to Scheme 2, only the *trans* isomer of hyponitrous acid is generated. In fact, it appears that *cis*-hyponitrous acid is extremely unstable, and only indirect evidence for its existence has been collected.<sup>47,48</sup> This observation has been substantiated by DFT calculations (at the IEFPCM/B3LYP/6-311G(2d,d,p) level of theory). For example, the barrier of N<sub>2</sub>O elimination from *cis*-hyponitrous acid was calculated to be 74 kJ/mol,<sup>49</sup> whereas that of *trans*-hyponitrous acid was determined to be 98 kJ/mol, according to kinetic measurements.<sup>50</sup> It is thought that *cis*-hyponitrous acid is less stable kinetically because of nitrogen lone pair donation into the N-O σ\* bond, which results in a weakening of the N-O bond (Scheme 3), thereby lowering the barrier of N-O cleavage and, ultimately, facilitating N<sub>2</sub>O formation.<sup>51,52</sup> This phenomenon also likely explains the observation that transition metal *cis*-hyponitrite complexes are much more reactive than their *trans* counterparts (see below). Interestingly, though, *cis*-

hyponitrous acid is thermodynamically more stable than the *trans* isomer by 9.2 kJ/mol, according to calculations.<sup>51,52</sup>

**Scheme 3.** Interaction of the nitrogen lone pair with the N-O  $\sigma^*$  orbital on hyponitrous acid. Adapted from Reference <sup>52</sup>.



The barrier of *cis/trans* isomerization for hyponitrous acid has not been measured experimentally, but it has been calculated for the mono-anions,  $[\text{HONNO}]^-$ , and it was found to be substantial (226 kJ/mol).<sup>51</sup> As such, *cis/trans* isomerization is unlikely to occur at any reasonable rate at room temperature.<sup>51</sup> This observation is relatively easy to rationalize because isomerization would require the disruption of the N=N  $\pi$  bond. That said, there is evidence that ketones can catalyze the *cis/trans* isomerization of the mono-anions,  $[\text{HONNO}]^-$ ,<sup>53</sup> and so *cis/trans* isomerization could be relevant in some systems.

The preparation and characterization of the sodium salts of hyponitrous acid has also been extensively investigated. As mentioned above, *trans*- $\text{Na}_2\text{N}_2\text{O}_2$  can be prepared by reduction of sodium nitrite with Na / Hg amalgam in water at 0 °C (Scheme 2).<sup>43,44</sup> However, it can also be prepared by reaction of hydroxylamine with *n*-propyl nitrite in an ethanol/sodium ethoxide mixture (Scheme 4a).<sup>53,54</sup> It should be noted, however, that the reported yield for this transformation is poor (13.5%),<sup>54</sup> and some authors have

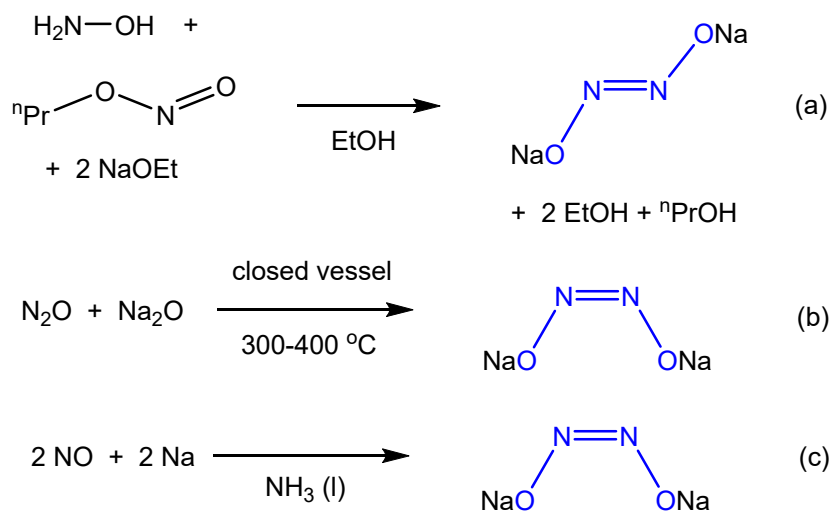


mentioned that the purity of the isolated product, when prepared via this route, is low.<sup>53</sup> *trans* sodium-hyponitrite has been structurally characterized as its penta-hydrate, *trans*-Na<sub>2</sub>N<sub>2</sub>O<sub>2</sub>·5H<sub>2</sub>O. As anticipated, it features a short N-N bond (1.256(2) Å), consistent with double bond character in the N-N interaction.<sup>45</sup> *trans*-hyponitrite has also been characterized extensively by vibrational spectroscopy.<sup>46,55-58</sup> The Raman spectrum of *trans*-Na<sub>2</sub>N<sub>2</sub>O<sub>2</sub> in water features an absorption at 1383 cm<sup>-1</sup>,<sup>56,58</sup> which is assignable to the N=N stretch. In contrast, the related *N,N,N',N'*-tetraethylethylenediamine salt, [Et<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>2</sub>N(H)Et<sub>2</sub>][N<sub>2</sub>O<sub>2</sub>], features an N=N stretch at 1448 cm<sup>-1</sup> in its Raman spectrum.<sup>45</sup> Consistent with its centrosymmetric structure, this vibration is not observed in the IR spectrum.

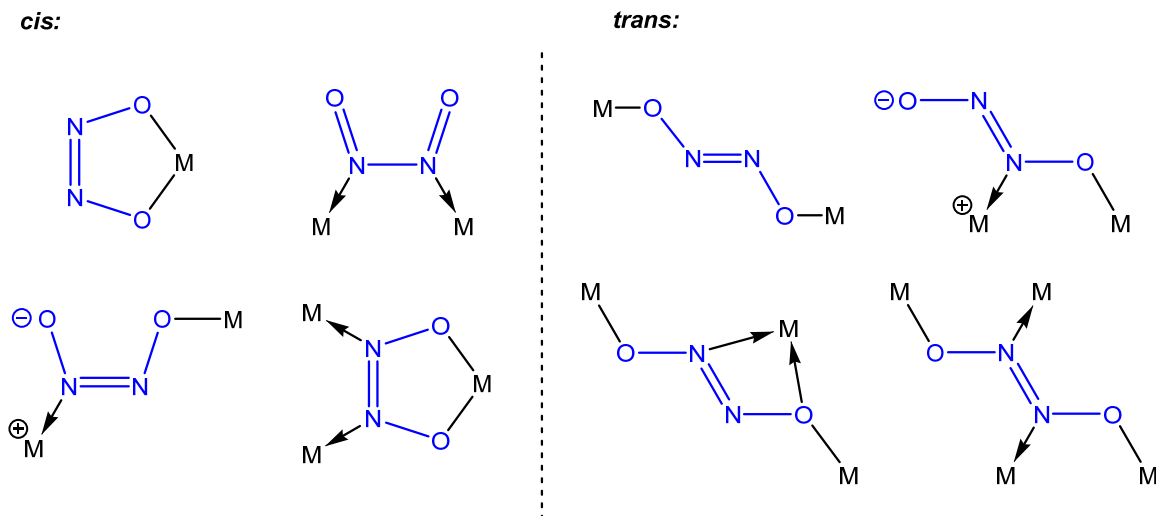
The sodium salt of *cis*-hyponitrite can be prepared by reaction of N<sub>2</sub>O with Na<sub>2</sub>O at high temperatures and pressures (Scheme 4b).<sup>59,60</sup> Alternately, it can be prepared by reduction of NO with Na in liquid ammonia (Scheme 4c),<sup>61,62</sup> although it should be noted that no yields were reported for this transformation. Interestingly, widely varying decomposition temperatures have been reported for *cis*-Na<sub>2</sub>N<sub>2</sub>O<sub>2</sub>,<sup>59,61,62</sup> which may reflect differences in material purity. Thus far, a single crystal X-ray diffraction analysis of *cis*-Na<sub>2</sub>N<sub>2</sub>O<sub>2</sub> has not been reported. Nonetheless, X-ray powder diffraction experiments and vibrational spectroscopy support the *cis* formulation.<sup>59-61</sup> According to X-ray powder diffraction, *cis*-Na<sub>2</sub>N<sub>2</sub>O<sub>2</sub> features an N-N bond length of 1.20(3) Å, similar to that observed for *trans*-Na<sub>2</sub>N<sub>2</sub>O<sub>2</sub>. The observation of an N-N stretch in both the IR (1320, 1329 cm<sup>-1</sup>) and Raman (1325 cm<sup>-1</sup>) spectra further support the *cis* formulation. Interestingly, and in contrast to hyponitrous acid, *trans*-hyponitrite is slightly more stable

than the *cis* isomer by 1.6 kJ/mol, according to DFT calculations (B3LYP functional using the aug-cc-pVTZ basis set).<sup>51</sup>

**Scheme 4.** Syntheses of the sodium salts of *trans*- and *cis*-hyponitrite.



**2.2. *cis*- and *trans*-hyponitrite coordination chemistry.** There are less than two dozen structurally characterized transition metal hyponitrite complexes reported in the literature. Despite this small sample size, the hyponitrite ligand has been shown to exhibit a rich variety of binding modes (Chart 1). Metal ions can coordinate and stabilize both the *cis*- and *trans*-isomers of hyponitrite. In addition, each isomer can bind up to four different metal centers. In this section, we present the synthetic procedures that have been used to prepare hyponitrite coordination compounds. The reactivity of these complexes will also be discussed. Excluded from the current discussion is the chemistry of *NO Reductase* and *flavodiiron NO reductase* model compounds, as several excellent reviews have covered their synthesis and reactivity in recent years.<sup>1,2,7,14,42</sup>

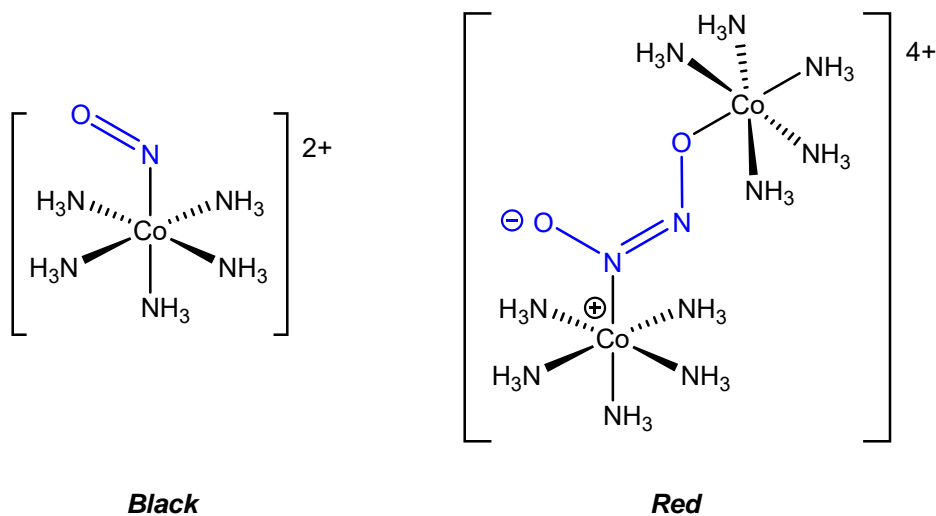


**Chart 1.** Known binding modes of the *cis*- and *trans*-hyponitrite ligands.

**2.2.1. Synthesis of the hyponitrite ligand from NO gas.** Metal mediated reductive coupling of two nitric oxide molecules has been used to prepare a hyponitrite complex in several instances. For example, in 1903 it was discovered that addition of NO gas to  $[\text{Co}(\text{NH}_3)_6]^{2+}$  yielded a material that could be isolated in either red (with  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , or  $\text{SO}_4^{2-}$  counterions) or black (with  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , or  $\text{IO}_3^-$  counterions) forms, depending on the identity of the counterion.<sup>63-65</sup> Interestingly, the black and red forms can both be isolated with the  $\text{NO}_3^-$  counterion. Their structures were not definitely determined for over 60 years. For example, in 1965, the black form was determined to be an octahedral mono-nitrosyl complex,  $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{2+}$ , by X-ray crystallography (Chart 2).<sup>66,67</sup> Subsequently, in 1969, the structure of the red form was determined by X-ray crystallography to be a bridged *cis*-hyponitrite complex,  $[(\text{H}_3\text{N})_5\text{Co}(\mu\text{-O,N-ONNO})\text{Co}(\text{NH}_3)_5][\text{NO}_3]_4$  (Chart 2), which features a novel  $\mu\text{-O,N}$  hyponitrite binding mode.<sup>68,69</sup> Very little is known about its mechanism of formation, but it seems likely that

it is generated via coupling of two  $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{2+}$  molecules. Formally, this represents the coupling of two  $\text{NO}^-$  ligands, and is similar to the reactivity exhibited by the 5-coordinate nickel nitrosyl,  $[\text{Ni}(\text{NO})(\text{bipy})_2]^+$ ,<sup>70,71</sup> whose chemistry will be discussed in the paragraphs below. Interestingly, addition of aqueous KCN to the black isomer,  $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{2+}$ , has been proposed to yield a *cis*-hyponitrite complex,  $\text{K}_6[\text{Co}_2(\text{CN})_{10}(\text{N}_2\text{O}_2)]$ .<sup>72</sup> However, the exact identity of this complex remains somewhat contentious, and others have proposed that the same reaction instead generates a *trans*-hyponitrite complex.<sup>73,74</sup> Finally,  $[(\text{H}_3\text{N})_5\text{Co}(\mu\text{-O},\text{N-ONNO})\text{Co}(\text{NH}_3)_5][\text{NO}_3]_4$  was shown to react with dilute acid to generate  $\text{N}_2\text{O}$ , albeit slowly, along with the Co(III) coordination complex,  $[\text{Co}(\text{NH}_3)_5\text{Cl}][\text{NO}_3]_2$ .<sup>75</sup>

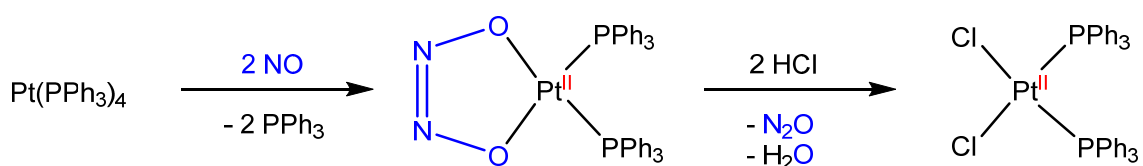
**Chart 2.** Structures of the black and red isomers of  $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{2+}$ .



The first structurally characterized monometallic *cis*- $[\text{N}_2\text{O}_2]^{2-}$  complex,  $(\text{Ph}_3\text{P})_2\text{Pt}(\kappa^2\text{-O}_2\text{N}_2)$ , was prepared by addition of NO gas to  $\text{Pt}(\text{PPh}_3)_4$  under air-free conditions (Scheme 5).<sup>76,77</sup> While its mechanism of formation is still unresolved, it is apparent that

the Pt center provides the two electrons needed to reductively couple two molecules of NO. In the solid state, the complex features a square planar geometry around the Pt center with a *cis*-hyponitrite ligand bound to Pt through its two oxygen atoms. The N=N (1.230(9) Å) and N–O bond lengths (1.370(8) and 1.363(8) Å) are consistent with a dianionic *cis*-hyponitrite ligand.<sup>78</sup> Interestingly,  $(\text{Ph}_3\text{P})_2\text{Pt}(\kappa^2\text{-O}_2\text{N}_2)$  reacts with dilute acids to release  $\text{N}_2\text{O}$  and generate  $\text{PtCl}_2(\text{PPh}_3)_2$ .<sup>76</sup> The hyponitrite complex is also sensitive to  $\text{O}_2$ , and reaction with adventitious oxygen results in formation of the nitrite complex,  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{NO}_2)_2$ .<sup>76</sup> Finally,  $(\text{Ph}_3\text{P})_2\text{Pt}(\kappa^2\text{-O}_2\text{N}_2)$  is unstable to light and decomposes when heated above 85 °C.<sup>78</sup> In contrast to the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with nitric oxide, reaction of  $\text{Pd}(\text{PPh}_3)_4$  with NO only results in formation of an un-identifiable solid.<sup>76</sup> However, when adventitious oxygen is present in the reaction mixture,  $(\text{Ph}_3\text{P})_2\text{Pd}(\text{NO}_2)_2$  is formed instead, suggesting a common intermediate in both the Pt and Pd reactions.<sup>76</sup> Additionally, NO gas is known to react with both  $\text{Ni}(\text{CO})_2(\text{PR}_3)_2$  and  $\text{Ni}(\text{CO})_4$ , and while the products have not been identified in these examples, it seems plausible that a hyponitrite complex is being generated, at least transiently.<sup>79,80</sup>

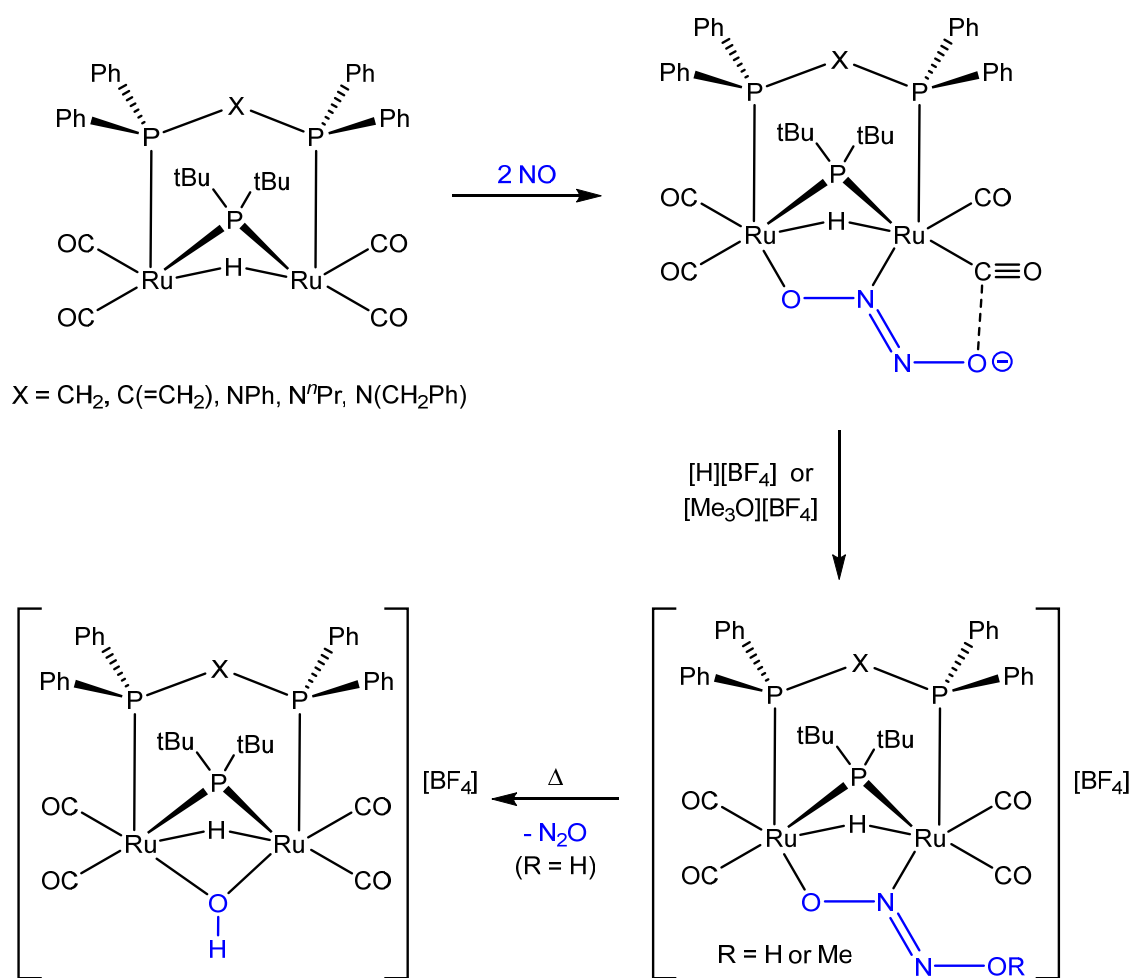
**Scheme 5.** Preparation of  $(\text{Ph}_3\text{P})_2\text{Pt}(\kappa^2\text{-O}_2\text{N}_2)$ .



Böttcher and co-workers reported that the bimetallic Ru(I) complexes,  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-L}_2)]$  ( $\mu\text{-L}_2 = \text{Ph}_2\text{PCH}_2\text{PPh}_2, \text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2, \text{Ph}_2\text{PN}(\text{Ph})\text{PPh}_2, \text{Ph}_2\text{PN}(\text{Pr}^i)\text{PPh}_2, \text{and Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{PPh}_2$ ), react with NO to yield the *trans*-hyponitrite complexes  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-L}_2)(\mu\text{-}\eta^2\text{-O,N-ONNO})]$ .<sup>81-83</sup> In these examples, the reducing equivalents required to couple two NO molecules come from the two Ru(I)

centers (one electron each). An X-ray crystallographic study of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-}\eta^2\text{-O,N-ONNO})]$  reveals that the *trans*-hyponitrite ligand bridges the two Ru metal centers via side-on coordination of an O–N bond (Scheme 6). The side-on bound N–O bond (1.355(2) Å) is slightly longer than the un-bound N–O bond (1.321(2) Å), while the N=N bond length is 1.267(2) Å. These metrical parameters support the presence of a doubly reduced hyponitrite ligand. Interestingly, this complex features a short contact between the unbound hyponitrite oxygen atom and an adjacent carbonyl ligand ( $\text{O}\cdots\text{C} = 2.244(4)$  Å).<sup>83</sup> This interaction is corroborated by the observation of a  $\nu(\text{CO})$  stretch of  $1742\text{ cm}^{-1}$  in the IR spectrum of this complex, which is significantly lower than its other terminal CO ligand stretches ( $1964\text{--}2035\text{ cm}^{-1}$ ).<sup>83</sup> DFT calculations (B3LYP level of theory using a Stuttgart/Dresden ECP (SDD) basis set for Ru) reveal that this interaction helps stabilize the *trans*-hyponitrite isomer by 8.8 kcal/mol vs. the *cis* isomer.<sup>81</sup>

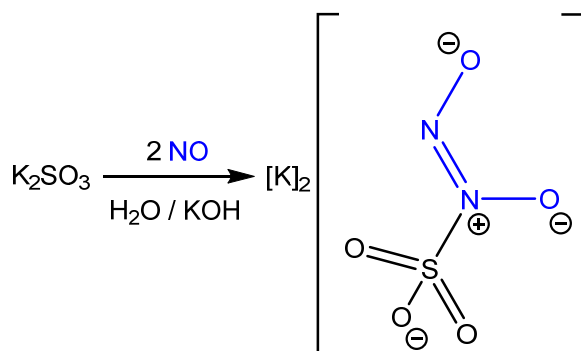
**Scheme 6.** Preparation and reactivity of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-L}_2)(\mu\text{-}\eta^2\text{-O,N-ONNO})]$



Electrophiles, such as H<sup>+</sup> and Me<sup>+</sup>, react at the unbound hyponitrite oxygen atom to yield [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-P<sup>t</sup>Bu<sub>2</sub>)(μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(μ-η<sup>2</sup>-ONNOH)][BF<sub>4</sub>] and [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-P<sup>t</sup>Bu<sub>2</sub>)(μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(μ-η<sup>2</sup>-ONNOMe)][BF<sub>4</sub>], respectively (Scheme 6).<sup>84</sup> Interestingly, thermolysis of [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-P<sup>t</sup>Bu<sub>2</sub>)(μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(μ-η<sup>2</sup>-ONNOH)][BF<sub>4</sub>], in ethanol, results in the loss of N<sub>2</sub>O and formation of a bridged hydroxide complex, [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-OH)(μ-P<sup>t</sup>Bu<sub>2</sub>)(μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)] [BF<sub>4</sub>]. The high temperature required for N<sub>2</sub>O release is consistent with the higher activation barrier for N–O bond cleavage calculated for the *trans*-N<sub>2</sub>O<sub>2</sub>H isomer, compared to its *cis*-N<sub>2</sub>O<sub>2</sub>H counterpart.<sup>51</sup>

Non-metal mediated reductive coupling of nitric oxide is also known. In particular, alkaline solutions of potassium sulphite are known to react with nitric oxide, forming potassium dinitrosulphite,  $[K_2][ON=N(O)SO_3]$  (Scheme 7),<sup>85-87</sup> also known as Pelouze's salt.<sup>88</sup> This material features a short N-N bond (1.279(4) Å) and a co-planar arrangement of the  $N_2O_2$  group.<sup>89,90</sup> Perhaps more importantly, it also features a *cis* arrangement of the hyponitrite moiety. As such, it could potentially function as a *cis*-hyponitrite transfer reagent, a class of materials for which very few examples exist (see Section 2.2.5).

**Scheme 7.** Synthesis of potassium dinitrosulphite



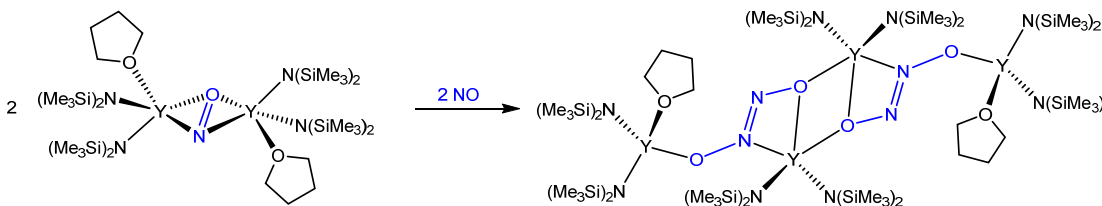
Finally, sequential addition of NO gas, at 20 Torr, to Co(TPP) (TPP = tetraphenylporphyrin) in toluene was proposed to generate the cobalt hyponitrite complex,  $[Co(TPP)(NO)(N_2O_2)]$ ;<sup>91</sup> however, this complex has not been structurally characterized. Additionally, Co(TPP) has been shown to catalyze the reduction of NO under a hydrogen atmosphere.<sup>92</sup>

**2.2.2. Synthesis of the hyponitrite ligand from a metal nitrosyl complex.** The reaction of NO gas with a pre-formed metal nitrosyl complex has also been used to prepare the hyponitrite moiety. For example, the yttrium complex,  $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu-\eta^2:\eta^2-NO)$ , which features the unusual doubly reduced  $NO^{2-}$  ligand, reacts with one equiv of



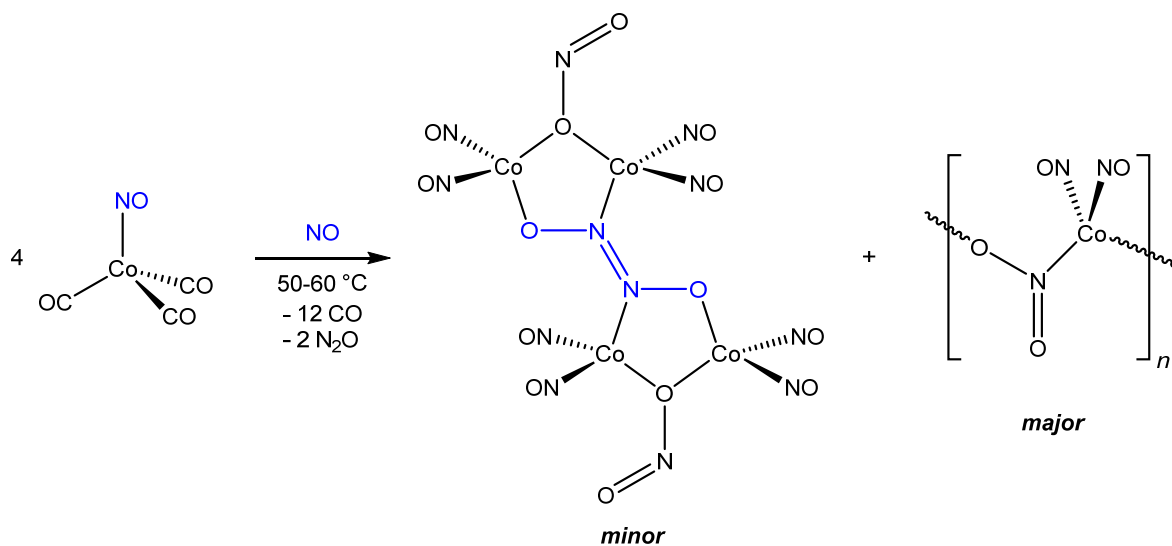
NO gas to yield the *trans*-hyponitrite complex,  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Y}\}_4(\mu_3\text{-ON=NO})_2(\text{THF})_2$  (Scheme 8).<sup>93</sup> The reaction likely proceeds via coupling of NO gas with the  $\text{NO}^{2-}$  ligand.

**Scheme 8.** Preparation of  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Y}\}_4(\mu_3\text{-ONNO})_2(\text{THF})_2$ .



Similarly, addition of NO gas to solid  $\text{Co}(\text{CO})_3(\text{NO})$  at 50-60 °C results in the formation of the cobalt hyponitrite complex,  $\text{Co}_4(\text{NO})_8(\text{NO}_2)_2(\textit{trans}\text{-N}_2\text{O}_2)$ , in low yields (Scheme 9), along with large amounts of the polymeric species  $[\text{Co}(\text{NO})_2(\text{NO}_2)]_n$ .<sup>94</sup> It seems likely that the hyponitrite ligand in the tetra-cobalt complex is formed by coupling of NO gas to a nitrosyl ligand; but given the complicated nature of this transformation, and its low yields, this assessment could be incorrect. In the solid-state, this complex features a *trans*-hyponitrite ligand with an unusual  $\kappa^4$  binding mode. The N=N bond length was determined to be 1.265 Å, consistent with the presence of an N=N double bond, while the N–O bond lengths were reported to be 1.316 Å.<sup>94</sup> Interestingly, pyrolysis of  $\text{Co}_4(\text{NO})_8(\text{NO}_2)_2(\text{N}_2\text{O}_2)$  yields both  $\text{N}_2\text{O}$  and NO as reaction products. Presumably, the  $\text{N}_2\text{O}$  is formed by decomposition of the hyponitrite ligand; however, it was noted that pyrolysis of  $[\text{Co}(\text{NO})_2(\text{NO}_2)]_n$  also yielded  $\text{N}_2\text{O}$  as a reaction product.<sup>94</sup>

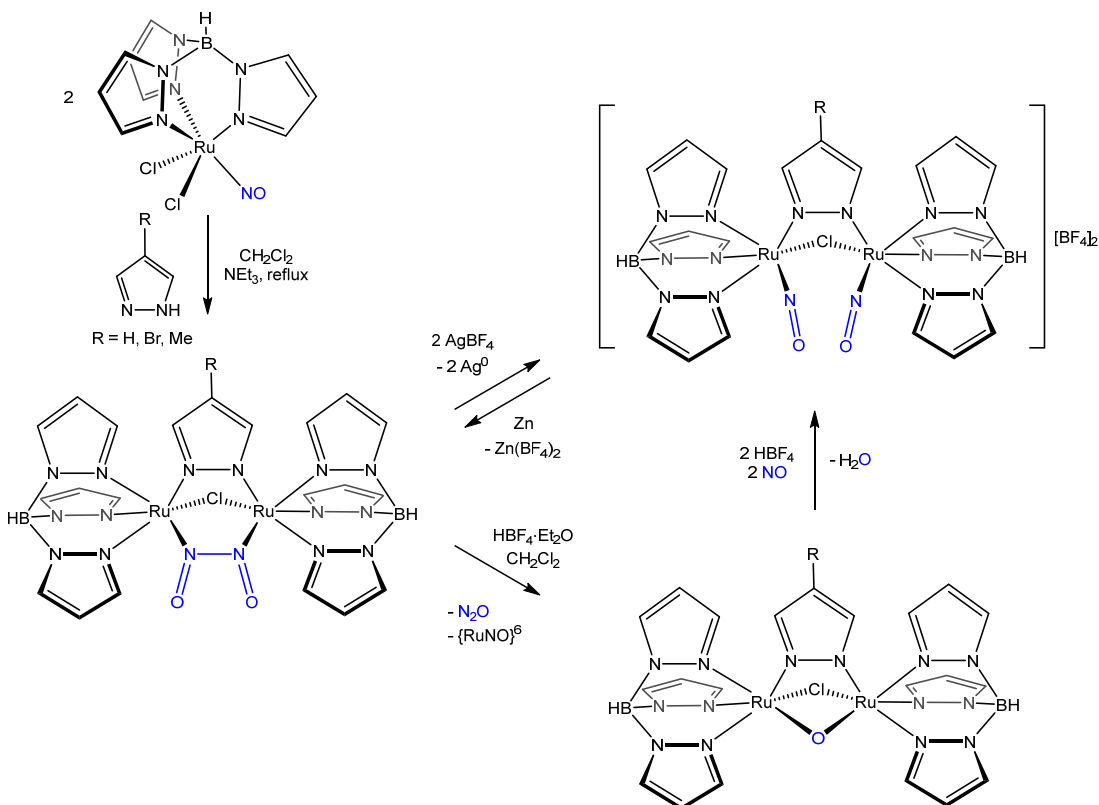
**Scheme 9.** Preparation of  $\text{Co}_4(\text{NO})_8(\text{NO}_2)_2(\text{N}_2\text{O}_2)$  and  $[\text{Co}(\text{NO})_2(\text{NO}_2)]_n$ .



The coupling of two metal nitrosyl ligands to form the hyponitrite fragment has also been observed. For example, Onishi and co-workers reported that heating a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{TpRuCl}_2(\text{NO})$ , in the presence of pyrazole and  $\text{NEt}_3$ , yielded a bimetallic Ru complex,  $(\text{TpRu})_2(\mu\text{-Cl})(\mu\text{-pz})\{\mu,\kappa^2\text{-N(=O)-N(=O)}\}$ .<sup>95</sup> Note that  $\text{NEt}_3$  is thought to function as a reducing agent in this transformation. This complex features an unprecedented neutral *cis*-hyponitrite ligand, e.g.,  $\text{O=N-N=O}$ , wherein the two Ru(II) centers are bridged by the nitrogen atoms of the hyponitrite moiety (Scheme 10). This oxidation state assignment is supported by both X-ray crystallographic studies and IR spectroscopic data. For example, the N–N distance in the *cis*-hyponitrite ligand (1.861(3) Å) is exceptionally long, consistent with very weak N–N single bond character. This distance is much longer than those typically observed for *cis*- or *trans*-hyponitrite (~1.25 Å). Additionally, the NO stretch observed in the IR spectrum is relatively high (1605  $\text{cm}^{-1}$ ) for a hyponitrite ligand and comparable to those observed for  $\text{NO}^-$  ligands.<sup>96</sup> DFT calculations (B3LYP level of theory using a LANL2DZ basis set for Ru) revealed that the highest occupied molecular orbital (HOMO) in this complex is primarily localized on the

N–N bond.<sup>95</sup> Significantly, the hyponitrite ligand in this complex is essentially identical to the (NO)<sub>2</sub> dimers proposed to form on metal surfaces during catalytic NO reduction.<sup>22</sup>

**Scheme 10.** Preparation of (TpRu)<sub>2</sub>(μ-Cl)(μ-pz){μ,κ<sup>2</sup>-N(=O)-N(=O)}.

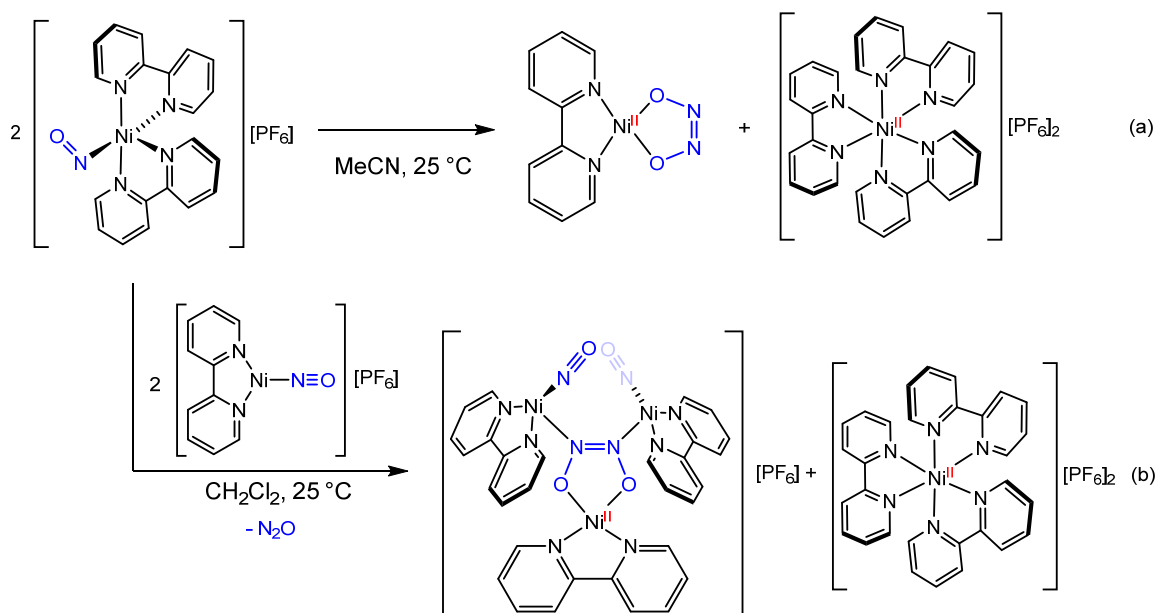


Oxidation of (TpRu)<sub>2</sub>(μ-Cl)(μ-pz){μ,κ<sup>2</sup>-N(=O)-N(=O)} by two electrons results in the cleavage of the N–N bond of the *cis*-hyponitrite ligand, and generation of the bimetallic dinitrosyl complex, [{TpRu(NO)}<sub>2</sub>(μ-Cl)(μ-pz)][BF<sub>4</sub>]<sub>2</sub> (Scheme 10). Reduction of this product with zinc metal results in the re-formation of (TpRu)<sub>2</sub>(μ-Cl)(μ-pz){μ,κ<sup>2</sup>-N(=O)-N(=O)}. Another noteworthy reaction is the addition of HBF<sub>4</sub>·OEt<sub>2</sub> to (TpRu)<sub>2</sub>(μ-Cl)(μ-pz){μ,κ<sup>2</sup>-N(=O)-N(=O)}, at room temperature, which results in rapid formation of nitrous oxide (25% yield). Several other products are also generated in this transformation, including the ruthenium oxo dimer, (TpRu)<sub>2</sub>(μ-Cl)(μ-pz)(μ-O), which was isolated in 21% yield, as well as the dinitrosyl complex, [{TpRu(NO)}<sub>2</sub>(μ-Cl)(μ-pz)](BF<sub>4</sub>)<sub>2</sub>, which was

isolated in 43 % yield (Scheme 10). This reactivity contrasts with that exhibited by the *trans*-hyponitrite ligand in the bimetallic Ru system reported by Böttcher (see above), in which the protonated hyponitrite complex could actually be isolated, and which only extruded nitrous oxide upon heating, consistent with the greater stability of *trans*- vs. *cis*-hyponitrite.<sup>84</sup> Finally, protonation of the ruthenium oxo complex, followed by treatment with NO gas, resulted in formation of the dinitrosyl complex, completing a *NO Reductase*-like catalytic cycle (Scheme 10).<sup>97</sup>

Another example of hyponitrite ligand formation from a well-defined metal nitrosyl complex was reported by our research group in 2012. In particular, we reported that, on standing at room temperature in MeCN, the five coordinate nickel nitrosyl complex,  $[\text{Ni}(\text{NO})(\text{bipy})_2][\text{PF}_6]$ , which features a bent  $\text{NO}^-$  ligand, cleanly converted into the *cis*-hyponitrite complex,  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$ , and  $[\text{Ni}(\text{bipy})_3][\text{PF}_6]_2$  (Scheme 11a).<sup>70</sup> The hyponitrite complex was characterized with both X-ray crystallography and IR spectroscopy. In the solid-state, it features a short  $\text{N}=\text{N}$  bond (1.240(3) Å), consistent with the presence of a dianionic *cis*-hyponitrite ligand. Similarly, its IR spectrum features absorptions at 937 and 1265  $\text{cm}^{-1}$ , which are assignable to the  $\text{N}-\text{O}$  and  $\text{N}=\text{N}$  stretches, respectively, of a dianionic *cis*-hyponitrite moiety.<sup>42</sup> We believe that the hyponitrite ligand in  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$  is formed by coupling of two  $\text{NO}^-$  ligands, and not by coupling of an  $\text{NO}^-$  ligand with either NO gas or an  $\text{NO}^+$  ligand. In an effort to support this hypothesis we performed a thorough mechanistic study on the formation of  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$ . These results are described in the paragraphs below.

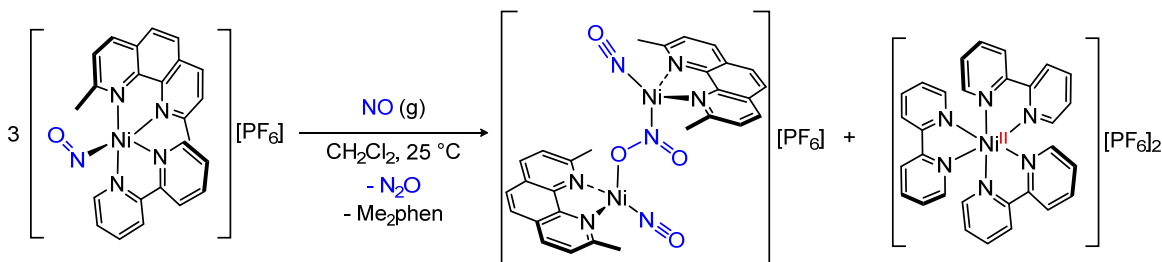
**Scheme 11.** Reactivity of  $[\text{Ni}(\text{NO})(\text{bipy})_2][\text{PF}_6]$ .



In an effort to evaluate whether the N=N bond in  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$  was formed by coupling of an  $\text{NO}^-$  ligand with an  $\text{NO}^+$  ligand, we performed the reaction of  $[\text{Ni}(\text{NO})(\text{bipy})_2][\text{PF}_6]$  with  $[\text{Ni}(\text{NO})(\text{bipy})][\text{PF}_6]$ , which serves as a source of  $\text{NO}^+$ . Interestingly, this transformation yielded the trimetallic *cis*-hyponitrite complex,  $[\{(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)\}\eta^1:\eta^1\text{-}N,N\text{-}\{\text{Ni}(\text{NO})(\text{bipy})\}_2][\text{PF}_6]_2$  (Scheme 11b). The *cis*-hyponitrite ligand in this complex features a novel  $\kappa^4$  binding mode, wherein the two oxygen atoms are bound to a single Ni center, while each nitrogen atom is capped by an  $[\text{Ni}(\text{NO})(\text{bipy})]^+$  fragment.<sup>71</sup> The interaction of the nitrogen atoms with the Ni centers has very little effect on the metrical parameters of the hyponitrite ligand. For example, its N–O bond lengths are 1.366(11) Å and 1.377(12) Å, while its N–N bond distance is 1.279(13) Å. These parameters are nearly identical to those exhibited by the hyponitrite ligand in  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$ .<sup>70</sup> We proposed that the hyponitrite ligand in  $[\{(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)\}\eta^1:\eta^1\text{-}N,N\text{-}\{\text{Ni}(\text{NO})(\text{bipy})\}_2][\text{PF}_6]_2$  was actually formed by coupling of two  $[\text{Ni}(\text{NO})(\text{bipy})_2][\text{PF}_6]$  complexes, resulting in the transient formation of  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$ . This complex then reacted with the strongly Lewis acidic  $[\text{Ni}(\text{NO})(\text{bipy})][\text{PF}_6]$ , to

generate the final product. Importantly, the formation of (bipy)Ni( $\kappa^2$ -O<sub>2</sub>N<sub>2</sub>) was thought to be completely independent of the added [Ni(NO)(bipy)][PF<sub>6</sub>].

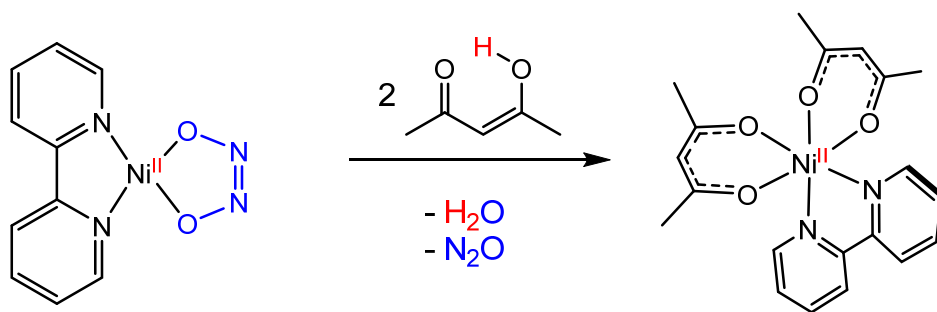
**Scheme 12.** Reactivity of [Ni(NO)(bipy)(Me<sub>2</sub>phen)][PF<sub>6</sub>].



We also explored the reaction of [Ni(NO)(bipy)<sub>2</sub>][PF<sub>6</sub>] with nitric oxide, in an effort to test whether the N=N bond in (bipy)Ni( $\kappa^2$ -O<sub>2</sub>N<sub>2</sub>) was formed by coupling of an NO<sup>-</sup> ligand with NO gas. Unfortunately, this reaction resulted in a complex mixture of products.<sup>71</sup> However, addition of NO gas to [Ni(NO)(bipy)(Me<sub>2</sub>phen)][PF<sub>6</sub>], which features a bulkier Me<sub>2</sub>phen ligand in place of one bipy ligand, cleanly yielded a bimetallic nickel nitrite complex, [Ni<sub>2</sub>(NO)<sub>2</sub>(Me<sub>2</sub>phen)<sub>2</sub>(bipy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>, along with [Ni(bipy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> and N<sub>2</sub>O (Scheme 12).<sup>71</sup> The presence of both N<sub>2</sub>O and the nitrite ligand in the reaction mixture is consistent with an NO disproportionation reaction and not NO reduction. Moreover, there was no evidence for the formation of a hyponitrite complex during the transformation. In fact, [Ni(NO)(bipy)(Me<sub>2</sub>phen)][PF<sub>6</sub>], unlike [Ni(NO)(bipy)<sub>2</sub>][PF<sub>6</sub>], is a thermally stable complex that is not susceptible to NO coupling, likely on account of its bulkier Me<sub>2</sub>phen ligand which prevents the close approach of two nitrosyl ligands. Given the abovementioned results, we concluded that there was little experimental support for either an NO<sup>-</sup>/NO<sup>+</sup> coupling mechanism or an NO<sup>-</sup>/NO<sup>•</sup> coupling mechanism, leaving the NO<sup>-</sup>/NO<sup>-</sup> coupling mechanism as the most reasonable explanation for hyponitrite formation in (bipy)Ni( $\kappa^2$ -O<sub>2</sub>N<sub>2</sub>).

Finally, we explored the reactivity of  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$ . Addition of acetylacetonone, a weak acid, to this complex resulted in clean formation of  $[\text{Ni}(\text{acac})_2(\text{bipy})][\text{PF}_6]$ , along with  $\text{N}_2\text{O}$  and water (Scheme 13).<sup>70</sup> Similar reactivity was observed for the platinum hyponitrite complex,  $(\text{Ph}_3\text{P})_2\text{Pt}(\kappa^2\text{-O}_2\text{N}_2)$ ,<sup>76</sup> and suggest that protonation of the hyponitrite ligand can trigger  $\text{N}_2\text{O}$  release. This hypothesis is also supported by calculations, which demonstrate that *cis*- $[\text{ONNOH}]^-$  has a much lower kinetic barrier to  $\text{N}_2\text{O}$  loss than the dianion, *cis*- $[\text{N}_2\text{O}_2]^{2-}$ .<sup>51</sup>

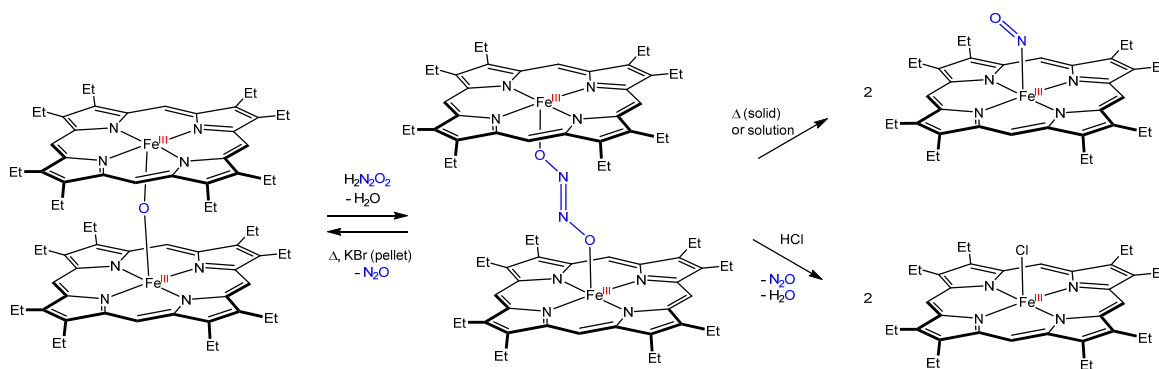
**Scheme 13.** Reactivity of  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$ .



### 2.2.3. Synthesis of the hyponitrite ligand from hyponitrous acid or its salts.

Surprisingly, there are only a few instances where *trans*-hyponitrous acid, or its salts, has been used as a hyponitrite synthon. In one example, addition of anhydrous *trans*-hyponitrous acid to  $[(\text{OEP})\text{Fe}]_2(\mu\text{-O})$  (OEP = octaethylporphyrin) resulted in formation of a bimetallic *trans*-hyponitrite complex,  $[(\text{OEP})\text{Fe}]_2(\mu\text{-O}_2\text{N}_2)$  (Scheme 14).<sup>98</sup> The dianionic nature of its hyponitrite ligand was confirmed by the short N=N bond (1.250(3) Å), as determined by X-ray crystallography. DFT calculations (BLYP functional) on relative energies of the *cis*- and *trans*-hyponitrite isomers of this complex reveal that they are nearly isoenergetic.<sup>98</sup>

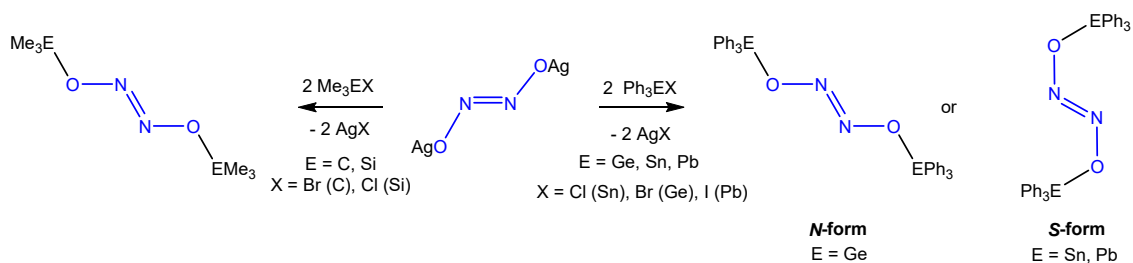
**Scheme 14.** Preparation and reactivity of  $[(\text{OEP})\text{Fe}]_2(\mu\text{-O}_2\text{N}_2)$ .



Interestingly, KBr pellets of  $[(\text{OEP})\text{Fe}]_2(\mu\text{-O}_2\text{N}_2)$  thermally decompose over the course of three hours, releasing  $\text{N}_2\text{O}$  and re-forming the bridged iron oxo complex.<sup>98</sup> In contrast, pure crystalline samples of  $[(\text{OEP})\text{Fe}]_2(\mu\text{-O}_2\text{N}_2)$  slowly convert into  $(\text{OEP})\text{FeNO}$ , via N–N bond cleavage.<sup>99</sup> This, of course, is the microscopic reverse of the N=N bond forming reaction proposed to occur during the coupling of two  $\text{NO}^-$  ligands to form hyponitrite.<sup>70,71</sup> The first order rate constant of N=N bond cleavage in  $\text{CH}_2\text{Cl}_2$  at 30 °C was determined to be  $6.4 \times 10^{-5} \text{ s}^{-1}$ , which corresponds to a kinetic barrier of 20  $\text{kcal}\cdot\text{mol}^{-1}$  for N=N bond formation. Interestingly, the rate of hyponitrite N=N bond cleavage in  $[(\text{OEP})\text{Fe}]_2(\mu\text{-O}_2\text{N}_2)$  can be increased significantly by addition of 500-fold excess of 1-methylimidazole. Under these conditions, the first order rate constant is  $1.2 \times 10^{-3} \text{ s}^{-1}$ .<sup>99</sup> These results suggest that Lewis base coordination to the Fe centers plays an important role in mediating the cleavage of the hyponitrite ligand in this system. Finally, addition of two equivalents of HCl to  $[(\text{OEP})\text{Fe}]_2(\mu\text{-O}_2\text{N}_2)$  yielded  $\text{N}_2\text{O}$ , along with two equivalents of  $(\text{OEP})\text{FeCl}$ ; reactivity that parallels that exhibited by several hyponitrite complexes, including  $(\text{bipy})\text{Ni}(\kappa^2\text{-O}_2\text{N}_2)$ .<sup>70,71</sup>

**Scheme 15.** Formation of group 14 *trans*-hyponitrite complexes.

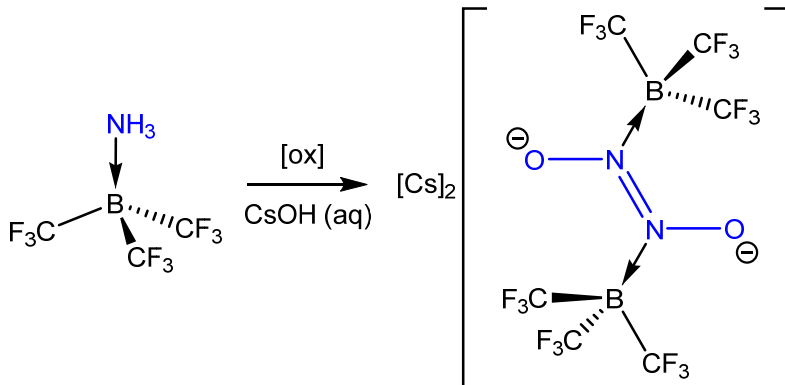




The silver salt of *trans*-hyponitrite, *trans*-Ag<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, has also been used for the preparation of a hyponitrite complex. For example, several group 14 *trans*-hyponitrite complexes have been prepared by reaction of Ph<sub>3</sub>EX (E = Ge, X = Br; E = Sn, X = Cl; E = Pb, X = I) with Ag<sub>2</sub>N<sub>2</sub>O<sub>2</sub> (Scheme 15).<sup>100-104</sup> All three compounds were characterized by X-ray crystallography, and not surprisingly, the *trans* arrangement of the hyponitrite moiety in *trans*-Ag<sub>2</sub>N<sub>2</sub>O<sub>2</sub> was retained in the product. Another noteworthy aspect of this chemistry is the orientation of the group 14 elements, which can occupy either an *N*- or *S*-conformation (Scheme 15).<sup>100,101</sup> Finally, the carbon derivative, Me<sub>3</sub>CON=NOCMe<sub>3</sub>, can be formed by reaction of Me<sub>3</sub>CBr with Ag<sub>2</sub>N<sub>2</sub>O<sub>2</sub> (Scheme 15). Interestingly, it is reported to decompose above 45 °C, generating *tert*-butoxy radicals via extrusion of N<sub>2</sub>.<sup>102</sup>

**2.2.4. Synthesis of the *trans*-hyponitrite ligand by oxidation of ammonia.** Bürger and co-workers reported that electrochemical oxidation of (CF<sub>3</sub>)<sub>3</sub>B(NH<sub>3</sub>) under basic conditions resulted in formation of the *trans*-hyponitrite complex, [Cs]<sub>2</sub>[(CF<sub>3</sub>)<sub>3</sub>B-N(O)=N(O)-B(CF<sub>3</sub>)<sub>3</sub>], in low yield (Scheme 16).<sup>105</sup> The N-N and N-O bond lengths in this complex are 1.30(2) and 1.30(1) Å, respectively, suggesting delocalization of the π-bond over all four atoms of the hyponitrite moiety. Given the low yield, and the unique nature of B(CF<sub>3</sub>)<sub>3</sub>, it is not clear if partial oxidation of bound NH<sub>3</sub> could become a general route to the hyponitrite moiety. Nonetheless, this result could inspire the development of other related routes to the hyponitrite ligand.

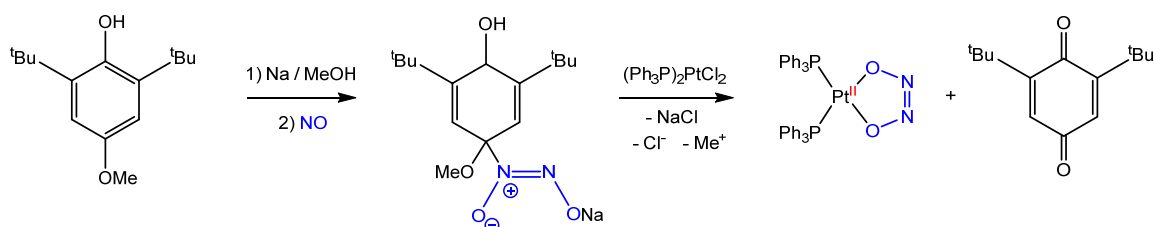
**Scheme 16.** Synthesis of  $[\text{Cs}]_2[(\text{CF}_3)_3\text{B}-\text{N}(\text{O})=\text{N}(\text{O})-\text{B}(\text{CF}_3)_3]$ .



**2.2.5. Synthesis of the *cis*-hyponitrite ligand from a diazeniumdiolate.** As is apparent from the sections above, *cis*-hyponitrite complexes have proven a challenge to generate rationally, which has hampered efforts to study their chemistry. Only a handful of complexes containing this ligand have been isolated, and most of these examples were formed serendipitously. To overcome this problem, efforts have been made to develop new synthetic protocols for generating this moiety. For example, Bohle and co-workers developed a novel cyclohexadienone diazeniumdiolate for use as a *cis*-hyponitrite synthon. This material can be synthesized by reaction of excess NO(g) with 2,6-di-*tert*-butyl-4-methoxy-phenol, under basic conditions (Scheme 17).<sup>106</sup> Reaction of its sodium salt with (Ph<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> yields the platinum *cis*-hyponitrite complex, (Ph<sub>3</sub>P)<sub>2</sub>Pt(*cis*-N<sub>2</sub>O<sub>2</sub>), concomitant with release of Me<sup>+</sup>, Cl<sup>-</sup>, and quinone (Scheme 17).<sup>78,107</sup> Several other group 10 di(chloride) precursors, including NiCl<sub>2</sub>(diphos), PtCl<sub>2</sub>(diphos), and PtCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>, also react with cyclohexadienone diazeniumdiolate to form the corresponding *cis*-hyponitrite complexes. While this method has proven to be reasonably general, it should be noted that there are still some mechanistic uncertainties surrounding this transformation. For one, the fate of the methyl cation has not been established. In addition, while it is certain that quinone by-product is being formed in the reaction, the

origin of its *para*-oxygen atom is not clear. It may be derived from the methoxy fragment, but Bohle and co-workers point out that the yields of the *cis*-hyponitrite complex drop precipitously when the reaction is performed in anhydrous media,<sup>78</sup> suggesting that the *para*-oxygen atom may also be derived from water.

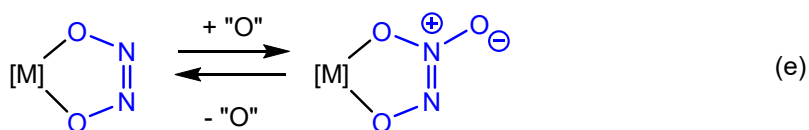
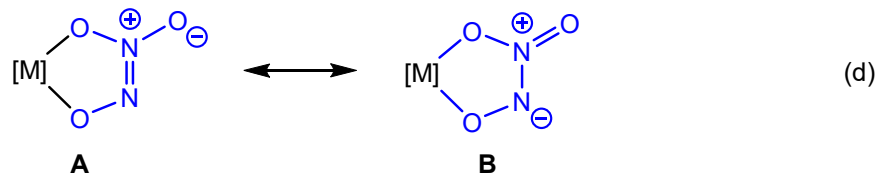
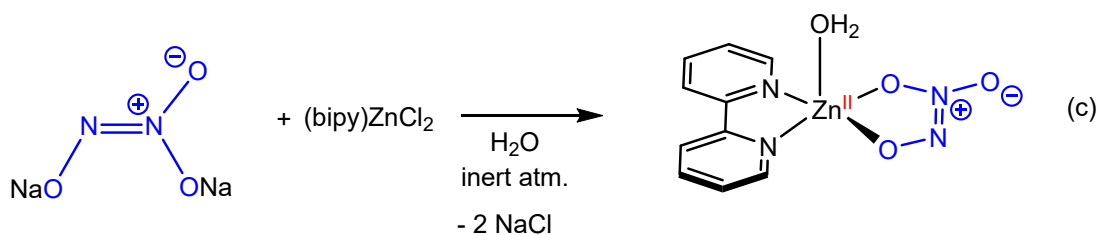
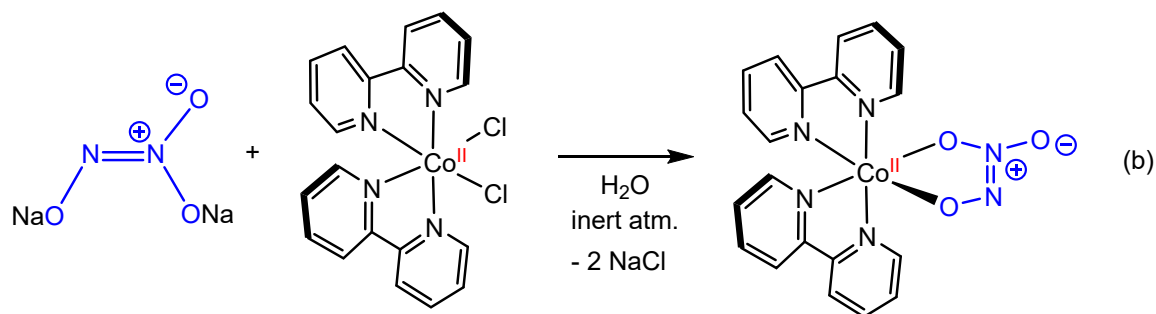
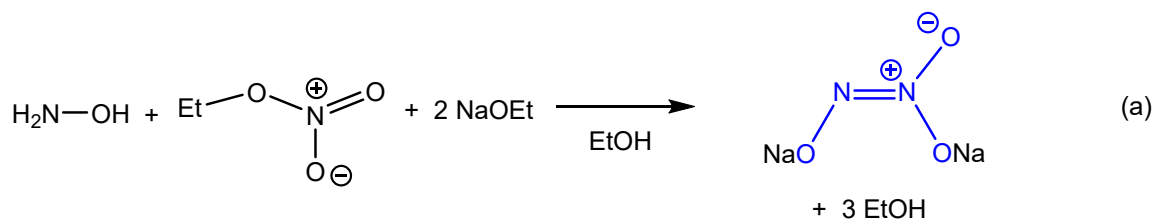
**Scheme 17.** Synthesis of cyclohexadienone diazeniumdiolate and its use as *cis*-hyponitrite synthon.



**2.2.6. Chemistry of Oxohyponitrite.** Any discussion of hyponitrite needs to include mention of the closely related nitrogen oxide, oxohyponitrite,  $[\text{N}_2\text{O}_3]^{2-}$ , also known as the trioxodinitrate anion,  $\alpha$ -oxohyponitrite, or Angeli's salt.<sup>108,109</sup> The chemistry of this anion is reasonably well established, and it is widely used as a HNO donor in *in vitro* studies.<sup>110-113</sup> It can be synthesized by reaction of hydroxylamine with ethylnitrate and sodium ethoxide (Scheme 18a),<sup>43,111,114</sup> a procedure that is similar to that reported for the synthesis of *trans*- $\text{Na}_2\text{N}_2\text{O}_2$  (Scheme 4a). Sodium trioxodinitrate can be isolated as its hydrate,  $\text{Na}_2\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,<sup>114</sup> which has been characterized by X-ray crystallography, but it can also be made in anhydrous form.<sup>43</sup> Curiously, its metal chemistry has not been widely explored, but there is some precedent for its ligation to a metal ion.<sup>108</sup> For example, the homoleptic trioxodinitrate complexes,  $[\text{Co}(\text{NH}_3)_6]_4[\text{M}(\text{N}_2\text{O}_3)_3]_3$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) have been reported,<sup>115</sup> but they have not been fully characterized. In addition, the mixed-ligand trioxodinitrate-bipyridine complexes,  $(\text{bipy})\text{Zn}(\text{N}_2\text{O}_3)(\text{H}_2\text{O})$  and  $(\text{bipy})_2\text{Co}(\text{N}_2\text{O}_3)$ , have been prepared (Scheme 18). Both complexes have been structurally characterized,

confirming their formulations. Interestingly, the N-N bond lengths for the zinc and cobalt derivatives are 1.280(5) and 1.333(11) Å, respectively. These values are slightly longer than those featured by the *trans*- and *cis*-hyponitrite moieties, suggesting a reduced bond order in the N-N interaction. The IR spectra of (bipy)Zn(N<sub>2</sub>O<sub>3</sub>)(H<sub>2</sub>O) and (bipy)<sub>2</sub>Co(N<sub>2</sub>O<sub>3</sub>) are also consistent with this reduced bond order. These observations can be explained by invoking an alternate resonance form of the oxohyponitrite ligand, **B** (Scheme 18d), which features a formal negative charge on one nitrogen atom and a N-N single bond.<sup>108</sup>

**Scheme 18.** Synthesis and coordination chemistry of oxohyponitrite anion.



In the greater context of *cis*-hyponitrite chemistry, the trioxodinitrate anion  $[\text{N}_2\text{O}_3]^{2-}$  could function as a *cis*-hyponitrite synthon, potentially providing a reliable synthetic route to this ephemeral moiety. For example, once ligated to the metal, selective removal of an oxygen atom from  $[\text{N}_2\text{O}_3]^{2-}$  would generate the *cis*-hyponitrite ligand. This could

be achieved, for example, by reaction with an O-atom acceptor such as  $\text{Ph}_3\text{P}$  (Scheme 18e).

### 3. Summary and Outlook

The last decade has seen considerable improvement in our understanding of  $\text{NO}_x$  reduction, both for biological systems and heterogeneous catalysts. Several lines of evidence, including *in situ* catalyst monitoring, computational modelling, and coordination chemistry reactivity studies, point to the intermediacy of *cis*-hyponitrite in these reactions. However, there are still many unanswered questions in regards to hyponitrite reactivity, as a systematic study of this ligand has never been performed. This is due, in part, to the lack of a rational, and widely applicable, method for the synthesis of hyponitrite complexes. In support of this observation, it is clear that most of the hyponitrite complexes discussed in this review were formed by chance. Thus, the development of new hyponitrite synthons is of particular importance, as this would allow for a systematic study of hyponitrite reactivity. The development of earth abundant catalysts for  $\text{NO}_x$  reduction is also of considerable interest. Most homogenous catalysts employ noble metals;<sup>116-118</sup> however, with an improved knowledge of hyponitrite reactivity it may be possible to develop a homogenous, earth abundant, NO reduction catalyst. In this regard, the aforementioned importance of the *cis*-hyponitrite ligand in NO reduction can be used as a guide for ligand choice. Specifically, a co-ligand that enforce two open coordination sites in a mutually *cis* orientation appears to be an important attribute. Once developed, these NO reduction catalysts would likely provide unique insights into the N=N bond forming step, knowledge that may be transferable to the mechanisms of both *NO Reductase* and heterogeneous  $\text{NO}_x$  reduction catalysts.

## **AUTHOR INFORMATION**

Corresponding Author

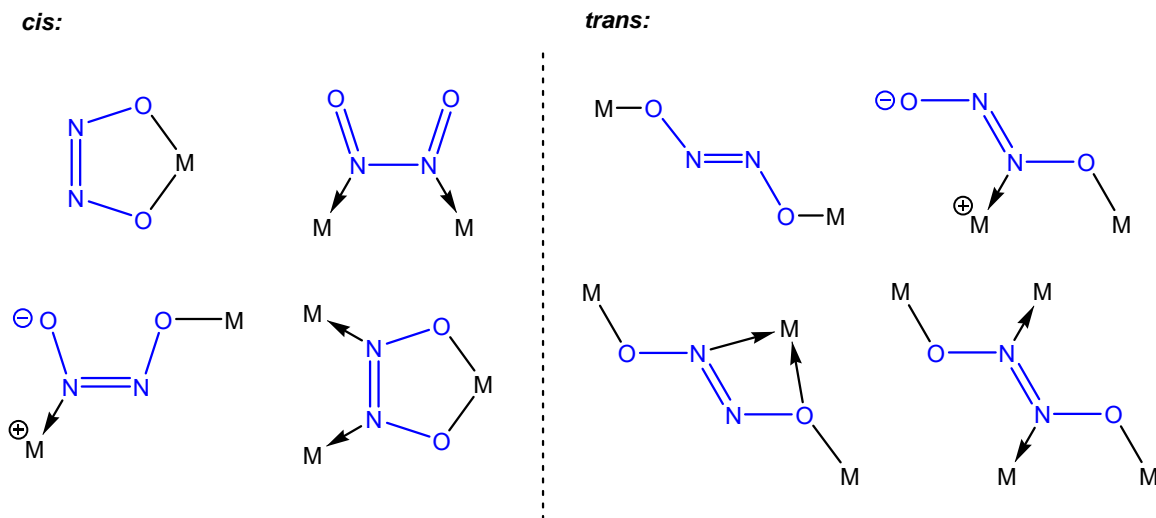
\*Email: hayton@chem.ucsb.edu

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## TOC Graphic

### Hyponitrite binding modes



**TOC Synopsis:** There are less than two dozen structurally characterized transition metal hyponitrite complexes reported in the literature. Yet, despite this small sample size, the hyponitrite ligand has been shown to exhibit a rich variety of binding modes.



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