Inorganic Chemistry
Forum Article
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Understanding the Role of Hyponitrite in Nitric Oxide Reduction

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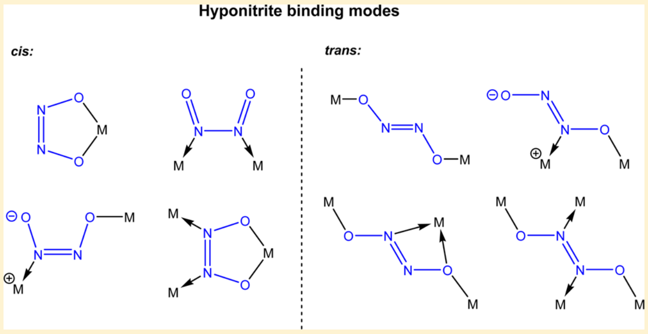
ABSTRACT: Herein, we review the preparation and coordination chemistry of cis and trans isomers of hyponitrite, $[N_2O_2]^{2-}$. Hyponitrite is known to bind to metals via a variety of bonding modes. In fact, at least eight different bonding modes have been observed, which is remarkable for such a simple ligand. More importantly, it is apparent that the cis isomer of hyponitrite is more reactive than the trans isomer because the barrier of N_2O elimination from *cis*-hyponitrite is lower than that of *trans*-hyponitrite. This observation may have important mechanistic implications for both heterogeneous 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),[1−12] which convert 2 equiv of nitric oxide, two reducing equivalents, and two protons into N_2O 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_2O is formed.[5,7] As a result, there is much speculation and debate about how these enzymes operate;[13−15] however, a common intermediate to many of these mechanistic proposals is the hyponitrite moiety, $[N_2O_2]^{2-}$,[1,7,16] which is formed via the coupling of two nitric oxide molecules.

Nitric oxide reduction is also necessary for controlling NO_x emissions in automotive exhaust. In modern vehicles, this is done using a "three-way" catalytic converter.[17,18] The current catalysts work exceptionally well;[18] 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.[18−20] In addition, because of tightening regulatory requirements, there is concern that current catalyst systems will not be able to meet future NO_x emission standards, in both Europe and North America.[18] Even before these challenges were recognized, though, there had been considerable interest in understanding the mechanism of heterogeneous NO reduction in catalytic converters.[20−25] 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).[18,24−31] However, more recent experimental work suggests that an alternate mechanism could also be operative. In this pathway, NO reduction proceeds via a "hyponitrite-like" $(NO)_2$ dimer (Scheme 1b),[20,22,32−34] and, in fact, this intermediate has been detected directly with IR spectroscopy on Ag(111) at low temperatures (70 K).[22,35] $(NO)_2$ dimers have also been imaged on Cu(110) using scanning tunneling microscopy (STM),[33] and, more recently, evidence for the formation $(NO)_3$ trimers on Cu(111) at 6 K has been collected with STM.[36] Nitric oxide also forms dimers on Pd(111) under certain conditions, as revealed by in situ infrared reflection absorption spectroscopy.[37]

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

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, $[N_2O_2]^{2-}$, during the reduction of nitric oxide. This moiety is known to bind to metal ions to form discrete, well-defined coordination complexes,[42] suggesting a role for homogeneous model systems in the efforts to evaluate the proposed mechanisms of 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

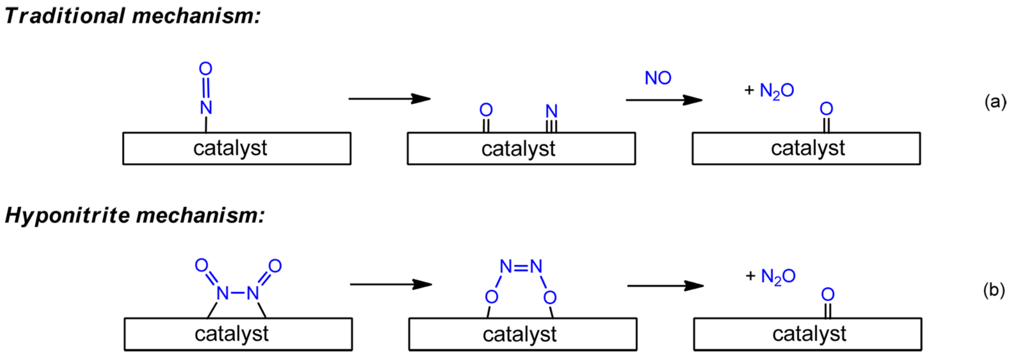
Special Issue: Small Molecule Activation: From Biological Principles to Energy Applications

Received: March 6, 2015
Published: April 30, 2015

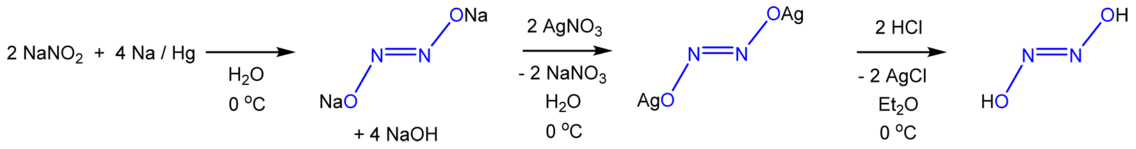
ACS Publications

DOI: 10.1021/acs.inorgchem.5b00516
Inorg. Chem. 2015, 54, 9330−9341

Scheme 1. Two Proposed Routes of NO_x Reduction on Metal Surfaces



Scheme 2. Synthesis of *trans*-Hyponitrous Acid



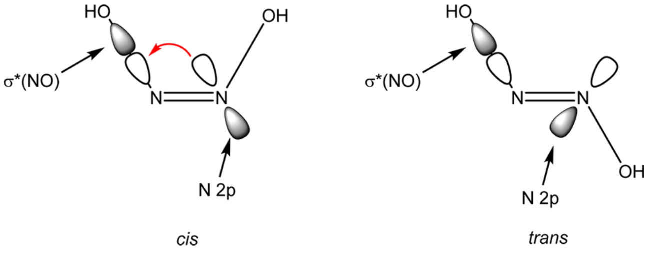
ions, and review its reactivity, in an effort to spur further development in this area.

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 (HONNOH), along with its salts. Anhydrous hyponitrous acid can be prepared in a multistep procedure from sodium nitrite. First, $NaNO_2$ is reduced with Na/Hg amalgam in water at 0 °C to generate sodium *trans*-hyponitrite (Scheme 2).[43−45] Sodium *trans*-hyponitrite is then reacted with an aqueous solution of $AgNO_3$, which results in precipitation of silver hyponitrite, $Ag_2N_2O_2$. Subsequent reaction of silver hyponitrite with anhydrous HCl in diethyl ether (Et_2O) results in the formation of *trans*-$H_2N_2O_2$ (Scheme 2),[45] which can be isolated as a white crystalline solid. Great care must be taken in handling solid hyponitrous acid because 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.[46] Interestingly, *trans*-hyponitrous acid was only recently characterized by X-ray crystallography.[45] It was found to cocrystallize within the salt $[HEt_2NCH_2CH_2NEt_2H][HN_2O_2]\cdot H_2N_2O_2$.[45] In the solid state, *trans*-hyponitrous acid features an N=N bond length of 1.226(4) Å, an N−O bond length of 1.363(3) Å, and an N−N−O angle of 109.9(3)°.[45] These parameters are similar to those featured by *trans*-hyponitrite (see below) and are consistent with the resonance structure shown in Scheme 2.

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.[47,48] 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_2O elimination from *cis*-hyponitrous acid was calculated to be 74 kJ/mol,[49] whereas that of *trans*-hyponitrous acid was determined to be 98 kJ/mol, according to kinetic measurements.[50] 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_2O formation.[51,52] 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.[51,52]

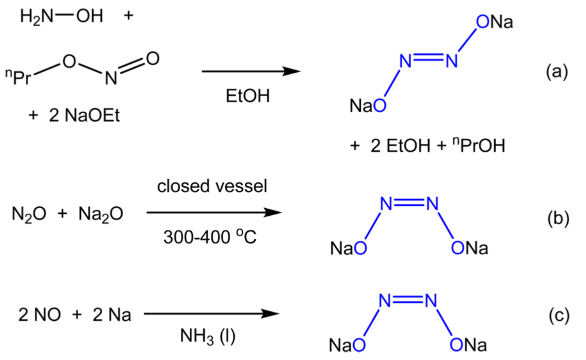
Scheme 3. Interaction of the Nitrogen Lone Pair with the N−O σ^* Orbital on Hyponitrous Acid (Adapted from Reference 52)



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

The preparation and characterization of sodium salts of hyponitrous acid has also been extensively investigated. As mentioned above, *trans*-$Na_2N_2O_2$ can be prepared by the reduction of sodium nitrite with Na/Hg amalgam in water at 0 °C (Scheme 2).[43,44] However, it can also be prepared by the reaction of hydroxylamine with *n*-propyl nitrite in an ethanol/sodium ethoxide mixture (Scheme 4a).[53,54] It should be noted, however, that the reported yield for this transformation is poor (13.5%),[54] and some authors have mentioned that the purity of the isolated product, when prepared via this route, is low.[53]

Scheme 4. Syntheses of the Sodium Salts of *trans*- and *cis*-Hyponitrite



Sodium *trans*-hyponitrite has been structurally characterized as its pentahydrate, *trans*-$Na_2N_2O_2 \cdot 5H_2O$. As anticipated, it features a short N−N bond [1.256(2) Å], consistent with double-bond character in the N−N interaction.[45] *trans*-Hyponitrite has also been characterized extensively by vibrational spectroscopy.[46,55−58] The Raman spectrum of *trans*-$Na_2N_2O_2$ in water features an absorption at 1383 cm^{-1},[56,58] which is assignable to the N=N stretch. In contrast, the related *N*,*N*,*N*′,*N*′-tetraethylethylenediamine salt, $[Et_2N(H)CH_2CH_2N(H)Et_2][N_2O_2]$, features an N=N stretch at 1448 cm^{-1} in its Raman spectrum.[45] Consistent with its centrosymmetric structure, this vibration is not observed in the IR spectrum.

The sodium salt of *cis*-hyponitrite can be prepared by the reaction of N_2O with Na_2O at high temperatures and pressures (Scheme 4b).[59,60] Alternately, it can be prepared by the reduction of NO with Na in liquid ammonia (Scheme 4c),[61,62] although it should be noted that no yields were reported for this transformation. Interestingly, widely varying decomposition temperatures have been reported for *cis*-$Na_2N_2O_2$,[59,61,62] which may reflect differences in the material purity. Thus far, a single-crystal X-ray diffraction analysis of *cis*-$Na_2N_2O_2$ has not been reported. Nonetheless, powder X-ray diffraction experiments and vibrational spectroscopy support the cis formulation.[59−61] According to powder X-ray diffraction, *cis*-$Na_2N_2O_2$ features an N−N bond length of 1.20(3) Å, similar to that observed for *trans*-$Na_2N_2O_2$. The observation of an N−N stretch in both the IR (1320 and 1329 cm^{-1}) and Raman (1325 cm^{-1}) spectra further supports 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).[51]

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 NOR and FDP model compounds, as several excellent reviews have covered their synthesis and reactivity in recent years.[1,2,7,14,42]

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 the addition of NO gas to $[Co(NH_3)_6]^{2+}$ yielded a material that could be isolated in either red (with Br^-, I^-, NO_3^-, or SO_4^{2-} counterions) or black (with Cl^-, NO_3^-, or IO_3^- counterions) form, depending on the identity of the counterion.[63−65] Interestingly, the black and red forms can both be isolated with the 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 mononitrosyl complex, $[Co(NH_3)_5(NO)]^{2+}$, by X-ray crystallography (Chart 2).[66,67] Subsequently, in 1969, the structure of the red form was determined by X-ray crystallography to be a bridged *cis*-hyponitrite complex, $[(H_3N)_5Co(\mu\text{-}O,N\text{-}ONNO)Co(NH_3)_5][NO_3]_4$ (Chart 2), which features a novel *μ-O,N*-hyponitrite binding mode.[68,69] Very little is known about its mechanism of formation, but it seems likely that it is generated via the coupling of two $[Co(NH_3)_5(NO)]^{2+}$ molecules. Formally, this represents the coupling of two NO^- ligands and is similar to the reactivity exhibited by the five-coordinate nickel nitrosyl $[Ni(NO)(bipy)_2]^+$,[70,71] whose chemistry will be discussed in the paragraphs below. Interestingly, the addition of aqueous KCN to the black isomer, $[Co(NH_3)_5(NO)]^{2+}$, has been proposed to yield a *cis*-hyponitrite complex, $K_6[Co_2(CN)_{10}(N_2O_2)]$.[72] However, the exact identity of this complex remains somewhat contentious, and others have

Chart 1. Known Binding Modes of the *cis*- and *trans*-Hyponitrite Ligands

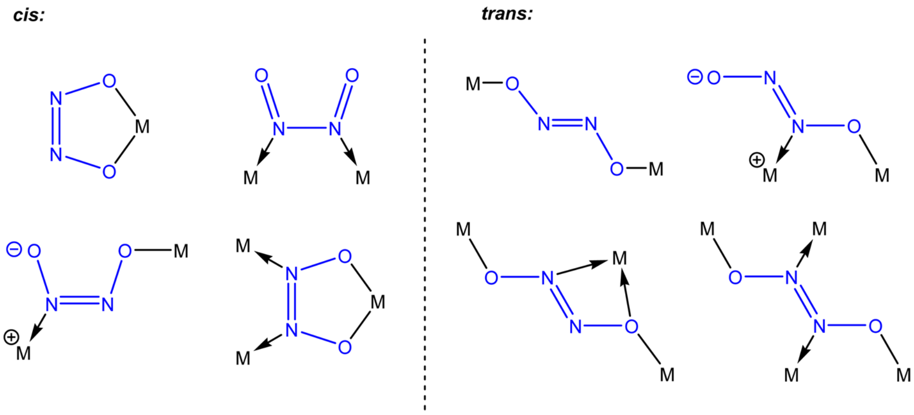
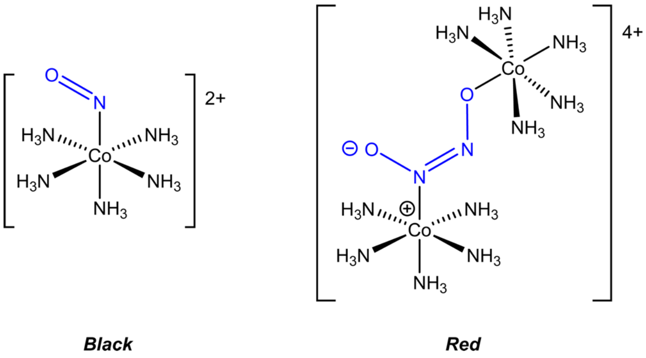


Chart 2. Structures of the Black and Red Isomers of $[Co(NH_3)_5(NO)]^{2+}$



Black *Red*

proposed that the same reaction instead generates a *trans*-hyponitrite complex.[73,74] Finally, $[(H_3N)_5Co(\mu\text{-}O,N\text{-}ONNO)Co(NH_3)_5][NO_3]_4$ was shown to react with dilute acid to generate N_2O, albeit slowly, along with the Co^{III} coordination complex, $[Co(NH_3)_5Cl][NO_3]_2$.[75]

The first structurally characterized monometallic *cis*-$[N_2O_2]^{2-}$ complex, $(Ph_3P)_2Pt(\kappa^2\text{-}O_2N_2)$, was prepared by the addition of NO gas to $Pt(PPh_3)_4$ under air-free conditions (Scheme 5).[76,77] 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 O atoms. The N═N [1.230(9) Å] and N−O [1.370(8) and 1.363(8) Å] bond lengths are consistent with a dianionic *cis*-hyponitrite ligand.[78] Interestingly, $(Ph_3P)_2Pt(\kappa^2\text{-}O_2N_2)$ reacts with dilute acids to release N_2O and generate $PtCl_2(PPh_3)_2$.[76] The hyponitrite complex is also sensitive to O_2, and reaction with adventitious oxygen results in formation of the nitrite complex $(Ph_3P)_2Pt(NO_2)_2$.[76] Finally, $(Ph_3P)_2Pt(\kappa^2\text{-}O_2N_2)$ is unstable to light and decomposes when heated above 85 °C.[78] In contrast to the reaction of $Pt(PPh_3)_4$ with nitric oxide, the reaction of $Pd(PPh_3)_4$ with NO only results in formation of an unidentifiable solid.[76] However, when adventitious oxygen is present in the reaction mixture, $(Ph_3P)_2Pd(NO_2)_2$ is formed instead, suggesting a common intermediate in both the Pt and Pd reactions.[76] Additionally, NO gas is known to react with both $Ni(CO)_2(PR_3)_2$ and $Ni(CO)_4$, and while the products have not been identified in these examples, it seems plausible that a hyponitrite complex is being generated, at least transiently.[79,80]

Böttcher and co-workers reported that the bimetallic Ru^I complexes $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}L_2)]$ (μ-L_2 = $Ph_2PCH_2PPh_2$, $Ph_2PC({=}CH_2)PPh_2$, $Ph_2PN(Ph)PPh_2$, $Ph_2PN(^nPr)PPh_2$, and $Ph_2PN(CH_2Ph)PPh_2$) react with NO to yield the *trans*-hyponitrite complexes $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}L_2)(\mu\text{-}\eta^2\text{-}O,N\text{-}ONNO)]$.[81−83] 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 $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}\eta^2\text{-}O,N\text{-}ONNO)]$ 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 unbound 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 dianionic hyponitrite ligand. Interestingly, this complex features a short contact between the unbound hyponitrite O atom and an adjacent carbonyl ligand [O···C = 2.244(4) Å].[83] This interaction is corroborated by the observation of a ν(CO) stretch of 1742 cm^{-1} in the IR spectrum of this complex, which is significantly lower than its other terminal CO ligand stretches (1964−2035 cm^{-1}).[83] DFT calculations [B3LYP level of theory using a Stuttgart/Dresden ECP (SDD) basis set for Ru] reveal that this interaction helps to stabilize the *trans*-hyponitrite isomer by 8.8 kcal/mol versus the cis isomer.[81]

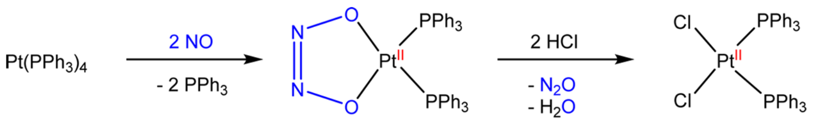
Electrophiles, such as H^+ and Me^+, react at the unbound hyponitrite O atom to yield $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}\eta^2\text{-}ONNOH)][BF_4]$ and $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}\eta^2\text{-}ONNOMe)][BF_4]$, respectively (Scheme 6).[84] Interestingly, thermolysis of $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}\eta^2\text{-}ONNOH)][BF_4]$, in ethanol, results in the loss of N_2O and formation of a bridged hydroxide complex, $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}P^tBu_2)(\mu\text{-}Ph_2PCH_2PPh_2)][BF_4]$. The high temperature required for N_2O release is consistent with the higher activation barrier for N−O bond cleavage calculated for the *trans*-N_2O_2H isomer, compared to its *cis*-N_2O_2H counterpart.[51]

Non-metal-mediated reductive coupling of nitric oxide is also known. In particular, alkaline solutions of potassium sulfite are known to react with nitric oxide, forming potassium dinitrososulfite, $[K_2][ON{=}N(O)SO_3]$ (Scheme 7),[85−87] also known as Pelouze's salt.[88] This material features a short N−N bond [1.279(4) Å] and a coplanar arrangement of the N_2O_2 group.[89,90] 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).

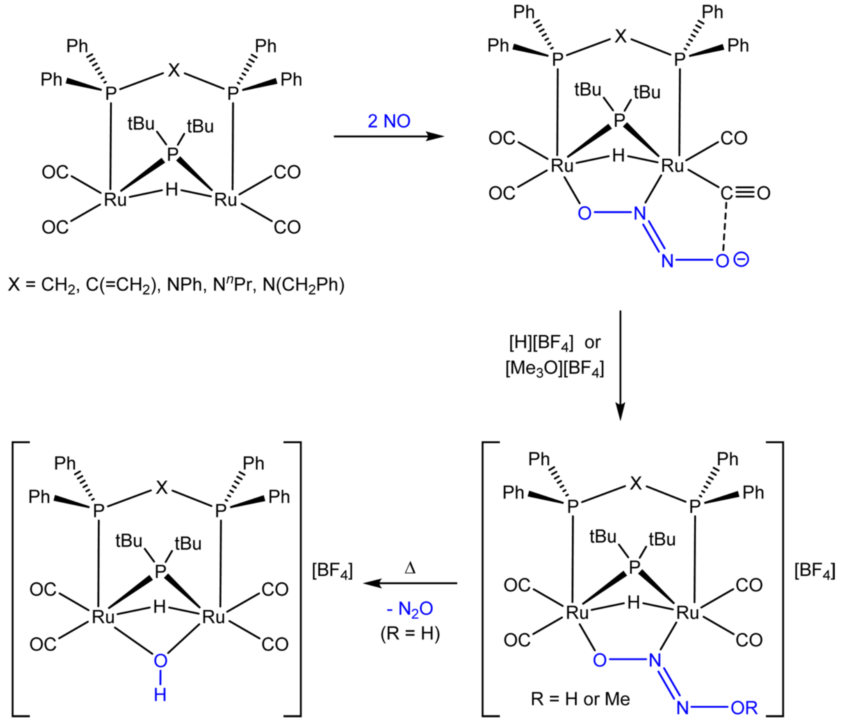
Finally, the sequential addition of NO gas, at 20 Torr, to Co(TPP) (TPP = tetraphenylporphyrin) in toluene was proposed to generate the cobalt hyponitrite complex $[Co(TPP)(NO)(N_2O_2)]$;[91] however, this complex has not been structurally characterized. Additionally, Co(TPP) has been shown to catalyze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

2.2.2. Synthesis of the Hyponitrite Ligand from a Metal Nitrosyl Complex. The reaction of NO gas with a preformed metal nitrosyl complex has also been used to prepare the hyponitrite moiety. For example, the yttrium complex $\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}NO)$, which features the unusual NO^{2-} ligand, reacts with 1 equiv of NO gas to yield the *trans*-hyponitrite complex $\{[(Me_3Si)_2N]_2Y\}_4(\mu_3\text{-}ON{=}NO)_2(THF)_2$ (Scheme 8).[93] The reaction likely proceeds via the coupling of NO gas with the NO^{2-} ligand.

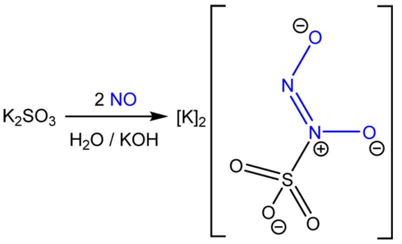
Scheme 5. Preparation of $(Ph_3P)_2Pt(\kappa^2\text{-}O_2N_2)$



Scheme 6. Preparation and Reactivity of $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}L_2)(\mu\text{-}\eta^2\text{-}O,N\text{-}ONNO)]$



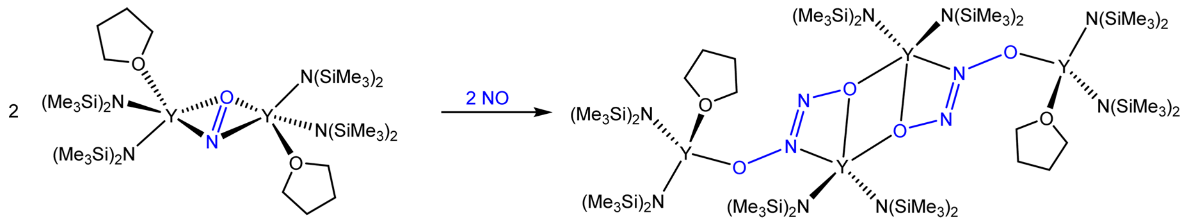
Scheme 7. Synthesis of Potassium Dinitrososulfite



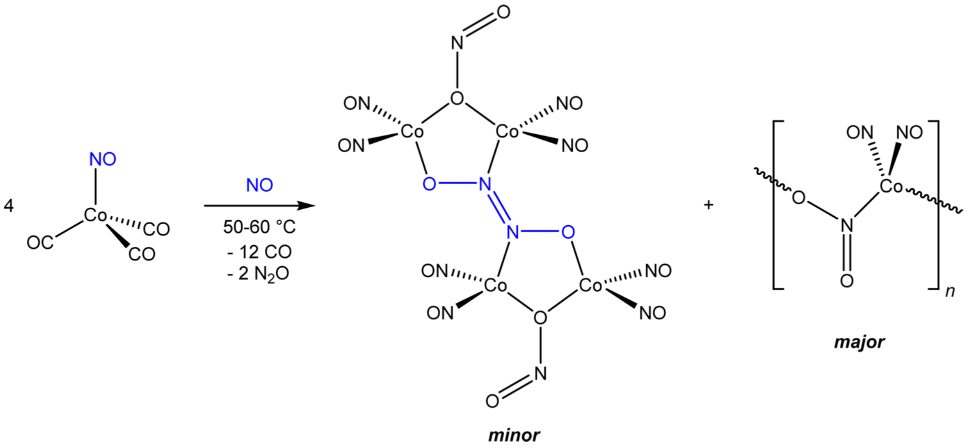
Similarly, the addition of NO gas to solid $Co(CO)_3(NO)$ at 50−60 °C results in formation of the cobalt hyponitrite complex $Co_4(NO)_8(NO_2)_2(trans\text{-}N_2O_2)$ in low yields (Scheme 9) along with large amounts of the polymeric species $[Co(NO)_2(NO_2)]_n$.[94] It seems likely that the hyponitrite ligand in the tetracobalt complex is formed by the 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 κ^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 length was reported to be 1.316 Å.[94] Interestingly, pyrolysis of $Co_4(NO)_8(NO_2)_2(N_2O_2)$ yields both N_2O and NO as reaction products. Presumably, the N_2O is formed by decomposition of the hyponitrite ligand; however, it was noted that pyrolysis of $[Co(NO)_2(NO_2)]_n$ also yielded N_2O as a reaction product.[94]

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 CH_2Cl_2 solution of $TpRuCl_2(NO)$, in the presence of pyrazole and NEt_3, yielded a bimetallic Ru complex, $(TpRu)_2(\mu\text{-}Cl)(\mu\text{-}pz)\{\mu,\kappa^2\text{-}N({=}O)N({=}O)\}$.[95] Note that NEt_3 is thought to function as a reducing agent in this transformation. This complex features an unprecedented neutral *cis*-hyponitrite ligand, e.g., O═N−N═O, wherein the two Ru^{II} centers are bridged by the N 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 cm^{-1}) for a hyponitrite ligand and comparable to those observed for NO^- ligands.[96] DFT calculations (B3LYP level of theory using a LANL2DZ basis set for Ru) revealed that the highest occupied molecular orbital in this complex is primarily localized on the N−N bond.[95] Significantly, the hyponitrite ligand in this

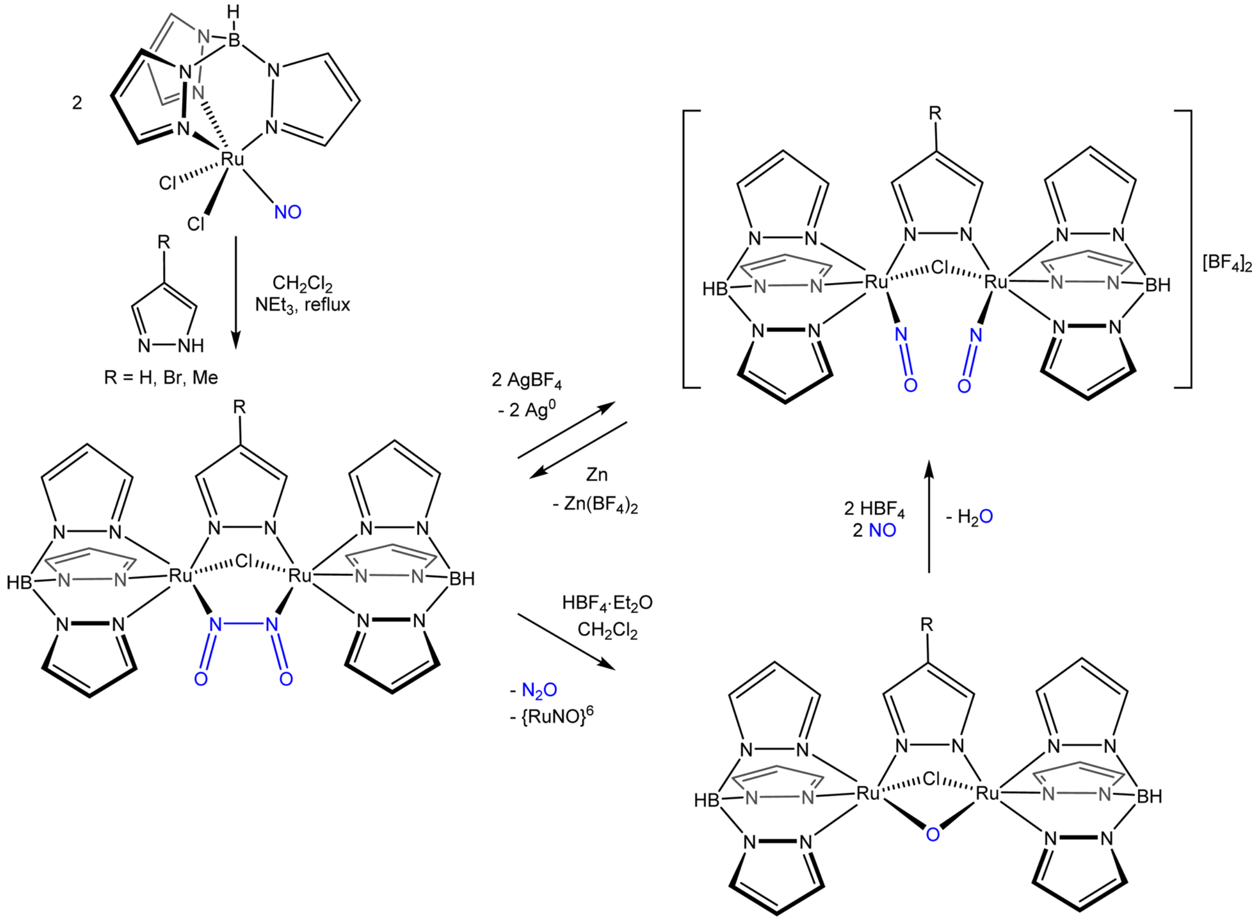
Scheme 8. Preparation of $\{[(Me_3Si)_2N]_2Y\}_4(\mu_3\text{-}ONNO)_2(THF)_2$



Scheme 9. Preparation of $Co_4(NO)_8(NO_2)_2(N_2O_2)$ and $[Co(NO)_2(NO_2)]_n$



Scheme 10. Preparation of $(TpRu)_2(\mu\text{-Cl})(\mu\text{-pz})\{\mu,\kappa^2\text{-N(=O)N(=O)}\}$



complex is essentially identical with the $(NO)_2$ dimers proposed to form on metal surfaces during catalytic NO reduction.[22]

Oxidation of $(TpRu)_2(\mu\text{-Cl})(\mu\text{-pz})\{\mu,\kappa^2\text{-N(=O)N(=O)}\}$ by two electrons results in cleavage of the N−N bond of the *cis*-hyponitrite ligand, and generation of the bimetallic dinitrosyl complex $[\{TpRu(NO)\}_2(\mu\text{-Cl})(\mu\text{-pz})][BF_4]_2$ (Scheme 10). Reduction of this product with Zn metal results in the re-formation of $(TpRu)_2(\mu\text{-Cl})(\mu\text{-pz})\{\mu,\kappa^2\text{-N(=O)N(=O)}\}$. Another noteworthy reaction is the addition of $HBF_4{\cdot}OEt_2$ to $(TpRu)_2(\mu\text{-Cl})(\mu\text{-pz})\{\mu,\kappa^2\text{-N(=O)N(=O)}\}$, at room temperature, which results in the rapid formation of nitrous oxide (25% yield). Several other products are also generated in this transformation, including the ruthenium oxo dimer $(TpRu)_2(\mu\text{-Cl})(\mu\text{-pz})(\mu\text{-O})$, which was isolated in 21% yield, as well as the dinitrosyl complex $[\{TpRu(NO)\}_2(\mu\text{-Cl})(\mu\text{-pz})](BF_4)_2$, 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 and co-workers (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*- versus *cis*-

DOI: 10.1021/acs.inorgchem.5b00516
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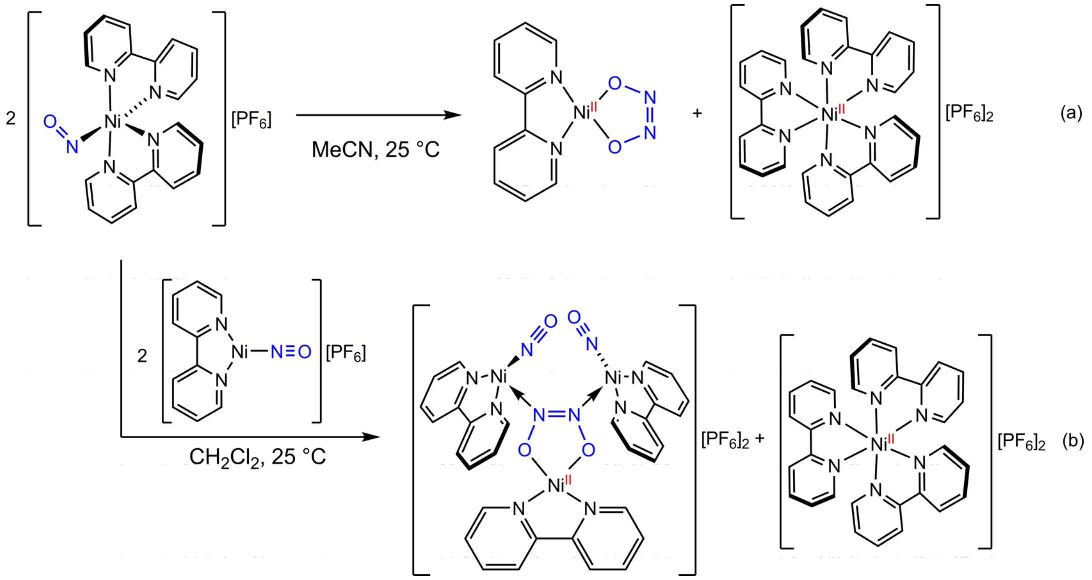
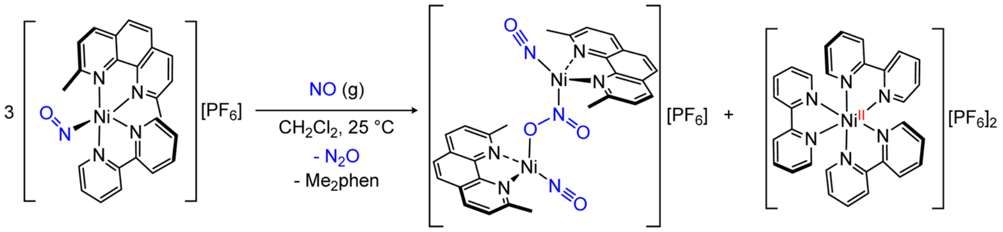
Scheme 11. Reactivity of $[Ni(NO)(bipy)_2][PF_6]$



Scheme 12. Reactivity of $[Ni(NO)(bipy)(Me_2phen)][PF_6]$



hyponitrite.[84] Finally, protonation of the ruthenium oxo complex, followed by treatment with NO gas, resulted in formation of the dinitrosyl complex, completing a NOR-like catalytic cycle (Scheme 10).[97]

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, upon standing at room temperature in MeCN, the five-coordinate nickel nitrosyl complex $[Ni(NO)(bipy)_2][PF_6]$, which features a bent NO^- ligand, cleanly converted into the *cis*-hyponitrite complex $(bipy)Ni(\kappa^2\text{-}O_2N_2)$ and $[Ni(bipy)_3][PF_6]_2$ (Scheme 11a).[70] The hyponitrite complex was characterized with both X-ray crystallography and IR spectroscopy. In the solid state, it features a short N═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 cm^{-1}, which are assignable to the N−O and N═N stretches, respectively, of a dianionic *cis*-hyponitrite moiety.[42] We believe that the hyponitrite ligand in $(bipy)Ni(\kappa^2\text{-}O_2N_2)$ is formed by the coupling of two NO^- ligands and not by the coupling of an NO^- ligand with either NO gas or an NO^+ ligand. In an effort to support this hypothesis, we performed a thorough mechanistic study on the formation of $(bipy)Ni(\kappa^2\text{-}O_2N_2)$. These results are described in the paragraphs below.

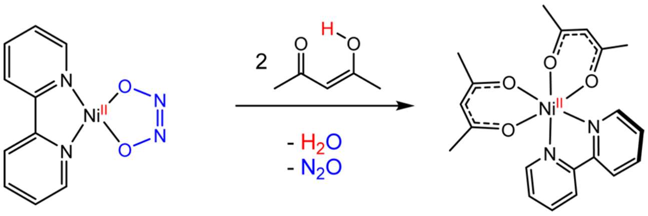
In an effort to evaluate whether the N═N bond in $(bipy)Ni(\kappa^2\text{-}O_2N_2)$ was formed by the coupling of an NO^- ligand with an NO^+ ligand, we performed the reaction of $[Ni(NO)(bipy)_2][PF_6]$ with $[Ni(NO)(bipy)][PF_6]$, which serves as a source of NO^+. Interestingly, this transformation yielded the trimetallic *cis*-hyponitrite complex $[\{(bipy)Ni(\kappa^2\text{-}O_2N_2)\}\eta^1{:}\eta^1\text{-}N,N\text{-}\{Ni(NO)(bipy)\}_2][PF_6]_2$ (Scheme 11b). The *cis*-hyponitrite ligand in this complex features a novel κ^4-binding mode, wherein the two O atoms are bound to a single Ni center, while each N atom is capped by an $[Ni(NO)(bipy)]^+$ fragment.[71] Interaction of the N 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) and 1.377(12) Å, while its N−N bond distance is 1.279(13) Å. These parameters are nearly identical with those exhibited by the hyponitrite ligand in $(bipy)Ni(\kappa^2\text{-}O_2N_2)$.[70] We proposed that the hyponitrite ligand in $[\{(bipy)Ni(\kappa^2\text{-}O_2N_2)\}\eta^1{:}\eta^1\text{-}N,N\text{-}\{Ni(NO)(bipy)\}_2][PF_6]_2$ was actually formed by the coupling of two $[Ni(NO)(bipy)_2][PF_6]$ complexes, resulting in the transient formation of $(bipy)Ni(\kappa^2\text{-}O_2N_2)$. This complex then reacted with the strongly Lewis acidic $[Ni(NO)(bipy)][PF_6]$ to generate the final product. Importantly, the formation of $(bipy)Ni(\kappa^2\text{-}O_2N_2)$ was thought to be completely independent of the added $[Ni(NO)(bipy)][PF_6]$.

We also explored the reaction of $[Ni(NO)(bipy)_2][PF_6]$ with nitric oxide in an effort to test whether the N═N bond in $(bipy)Ni(\kappa^2\text{-}O_2N_2)$ was formed by the coupling of an NO^- ligand with NO gas. Unfortunately, this reaction resulted in a complex mixture of products.[71] However, the addition of NO gas to $[Ni(NO)(bipy)(Me_2phen)][PF_6]$, which features a bulkier Me_2phen ligand in place of one bipy ligand, cleanly yielded a bimetallic nickel nitrite complex, $[\{(Me_2phen)Ni(NO)\}_2(\mu\text{-}\eta^1\text{-}N{:}\eta^1\text{-}O\text{-}NO_2)][PF_6]$, along with $[Ni(bipy)_3][PF_6]_2$ and N_2O (Scheme 12).[71] The presence of both N_2O 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_2phen)][PF_6], unlike [Ni(NO)$(bipy)_2$][PF_6], is a thermally stable complex that is not susceptible to NO coupling, likely because of its bulkier Me_2phen ligand, which prevents the close approach of two nitrosyl ligands. Given the above-mentioned results, we concluded that there was little experimental support for either an NO^-/NO^+ coupling mechanism or an $NO^-/NO^\bullet$ coupling mechanism, leaving the NO^-/NO^- coupling mechanism as the most reasonable explanation for hyponitrite formation in (bipy)Ni(κ^2-O_2N_2).

Finally, we explored the reactivity of (bipy)Ni(κ^2-O_2N_2). The addition of acetylacetone, a weak acid, to this complex resulted in the clean formation of [Ni$(acac)_2$(bipy)][PF_6], along with N_2O and water (Scheme 13).[70] Similar reactivity was observed for the platinum hyponitrite complex $(Ph_3P)_2$Pt(κ^2-O_2N_2)[76] and suggests that protonation of the hyponitrite ligand can trigger N_2O release. This hypothesis is also supported by calculations that demonstrate that *cis*-$[ONNOH]^-$ has a much lower kinetic barrier to N_2O loss than the dianion *cis*-$[N_2O_2]^{2-}$.[51]

Scheme 13. Reactivity of (bipy)Ni(κ^2-O_2N_2)



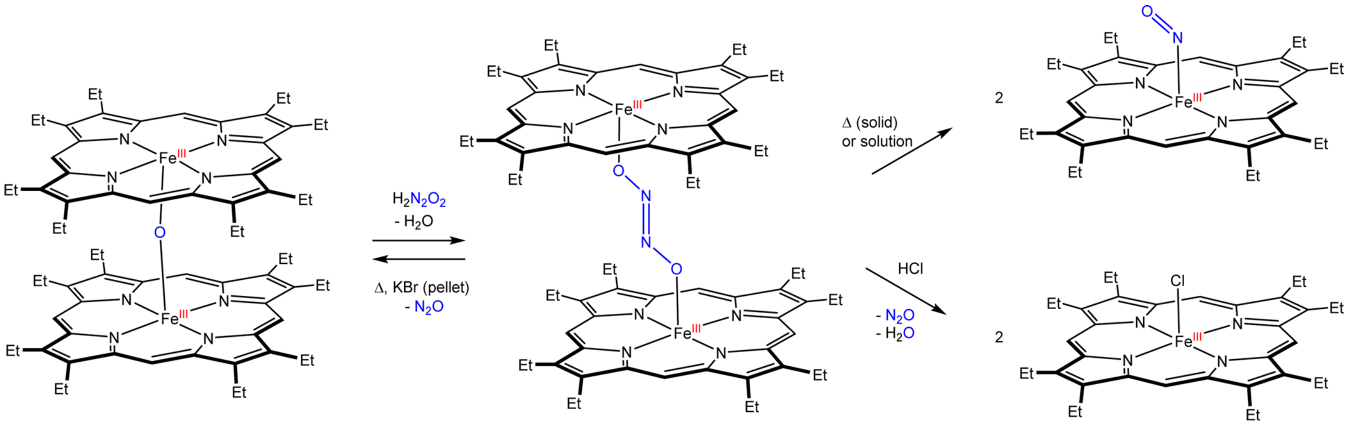
2.2.3. Synthesis of the Hyponitrite Ligand from Hyponitrous Acid or Its Salts. Surprisingly, there are only a few instances where *trans*-hyponitrous acid, or its salts, has been used as a hyponitrite synthon. In one example, the addition of anhydrous *trans*-hyponitrous acid to $[(OEP)Fe]_2$(μ-O) (OEP = octaethylporphyrin) resulted in the formation of a bimetallic *trans*-hyponitrite complex, $[(OEP)Fe]_2$(μ-O_2N_2) (Scheme 14).[98] 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 the relative energies of the *cis*- and *trans*-hyponitrite isomers of this complex reveal that they are nearly isoenergetic.[98]

Interestingly, KBr pellets of $[(OEP)Fe]_2$(μ-O_2N_2) thermally decompose over the course of 3 h, releasing N_2O and reforming the bridged iron oxo complex.[98] In contrast, pure crystalline samples of $[(OEP)Fe]_2$(μ-O_2N_2) slowly convert into (OEP)FeNO, via N−N bond cleavage.[99] This, of course, is the microscopic reverse of the N═N bond-forming reaction proposed to occur during the coupling of two NO^- ligands to form hyponitrite.[70,71] The first-order rate constant of N═N bond cleavage in CH_2Cl_2 at 30 °C was determined to be 6.4 × 10^{-5} s^{-1}, which corresponds to a kinetic barrier of 20 kcal/mol for N═N bond formation. Interestingly, the rate of hyponitrite N═N bond cleavage in $[(OEP)Fe]_2$(μ-O_2N_2) can be increased significantly by the addition of a 500-fold excess of 1-methylimidazole. Under these conditions, the first-order rate constant is 1.2 × 10^{-3} s^{-1}.[99] These results suggest that Lewis base coordination to the Fe centers plays an important role in mediating cleavage of the hyponitrite ligand in this system. Finally, the addition of 2 equiv of HCl to $[(OEP)Fe]_2$(μ-O_2N_2) yielded N_2O, along with 2 equiv of (OEP)FeCl, reactivity that parallels that exhibited by several hyponitrite complexes, including (bipy)Ni(κ^2-O_2N_2).[70,71]

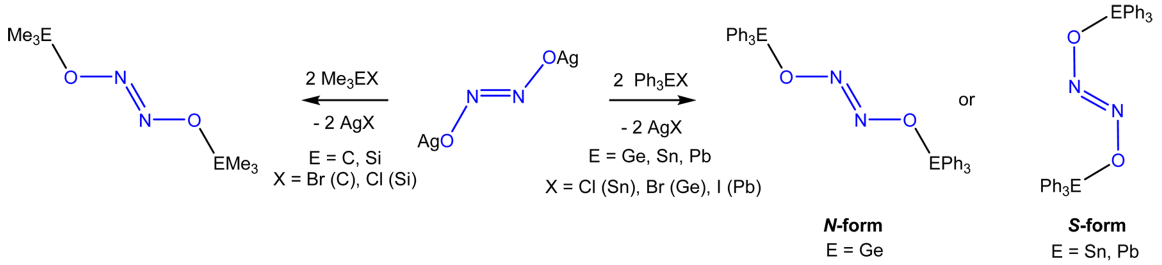
The silver salt of *trans*-hyponitrite, *trans*-$Ag_2N_2O_2$, has also been used for the preparation of a hyponitrite complex. For example, several group 14 *trans*-hyponitrite complexes have been prepared by the reaction of Ph_3EX (E = Ge, X = Br; E = Sn, X = Cl; E = Pb, X = I) with $Ag_2N_2O_2$ (Scheme 15).[100−104] All three compounds were characterized by X-ray crystallography, and, not surprisingly, the trans arrangement of the hyponitrite moiety in *trans*-$Ag_2N_2O_2$ 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).[100,101] Finally, the C derivative Me_3CON═NOCMe_3 can be formed by the reaction of Me_3CBr with $Ag_2N_2O_2$ (Scheme 15). Interestingly, it is reported to decompose above 45 °C, generating *tert*-butoxy radicals via extrusion of N_2.[102]

2.2.4. Synthesis of the trans-Hyponitrite Ligand by Oxidation of Ammonia. Bürger and co-workers reported that the electrochemical oxidation of $(CF_3)_3B(NH_3)$ under basic conditions resulted in formation of the *trans*-hyponitrite complex $[Cs]_2[(CF_3)_3$BN(O)═N(O)B$(CF_3)_3]$ in low yield (Scheme 16).[105] The N−N and N−O bond lengths in this complex are 1.30(2) and 1.30(1) Å, respectively, suggesting

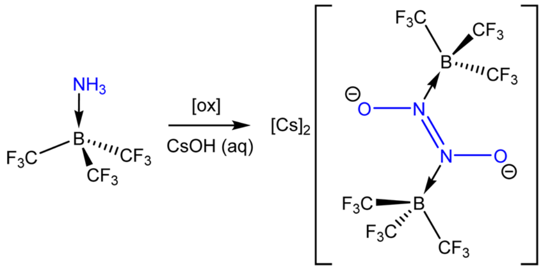
Scheme 14. Preparation and Reactivity of $[(OEP)Fe]_2$(μ-O_2N_2)



Scheme 15. Formation of Group 14 *trans*-Hyponitrite Complexes



Scheme 16. Synthesis of $[Cs]_2[(CF_3)_3BN(O)=N(O)B(CF_3)_3]$

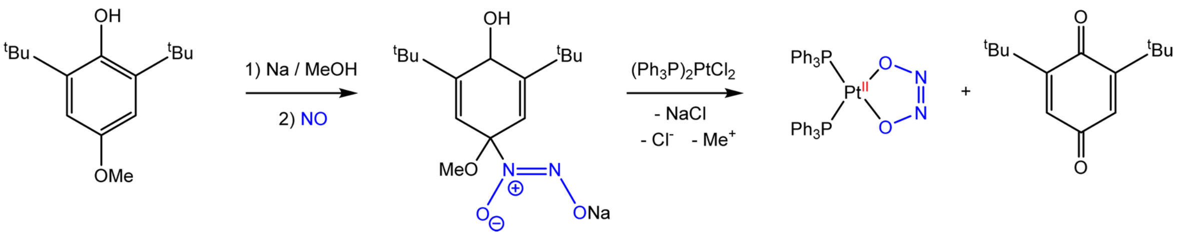


delocalization of the π bond over all four atoms of the hyponitrite moiety. Given the low yield and the unique nature of $B(CF_3)_3$, it is not clear if partial oxidation of bound NH_3 could become a general route to the hyponitrite moiety. Nonetheless, this result could inspire the development of other related routes to the hyponitrite ligand.

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 Imonigie developed a novel cyclohexadienone diazeniumdiolate for use as a *cis*-hyponitrite synthon. This material can be synthesized by the reaction of excess NO gas with 2,6-di-*tert*-butyl-4-methoxyphenol, under basic conditions (Scheme 17).[106] The reaction of its sodium salt with $(Ph_3P)_2PtCl_2$ yields the platinum *cis*-hyponitrite complex $(Ph_3P)_2Pt(cis\text{-}N_2O_2)$, concomitant with release of Me^+, Cl^-, and quinone (Scheme 17).[78,107] Several other group 10 dichloride precursors, including $NiCl_2$(diphos), $PtCl_2$(diphos), and $PtCl_2(PMePh_2)_2$, 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 byproduct 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,[78] suggesting that the *para*-oxygen atom may also be derived from water.

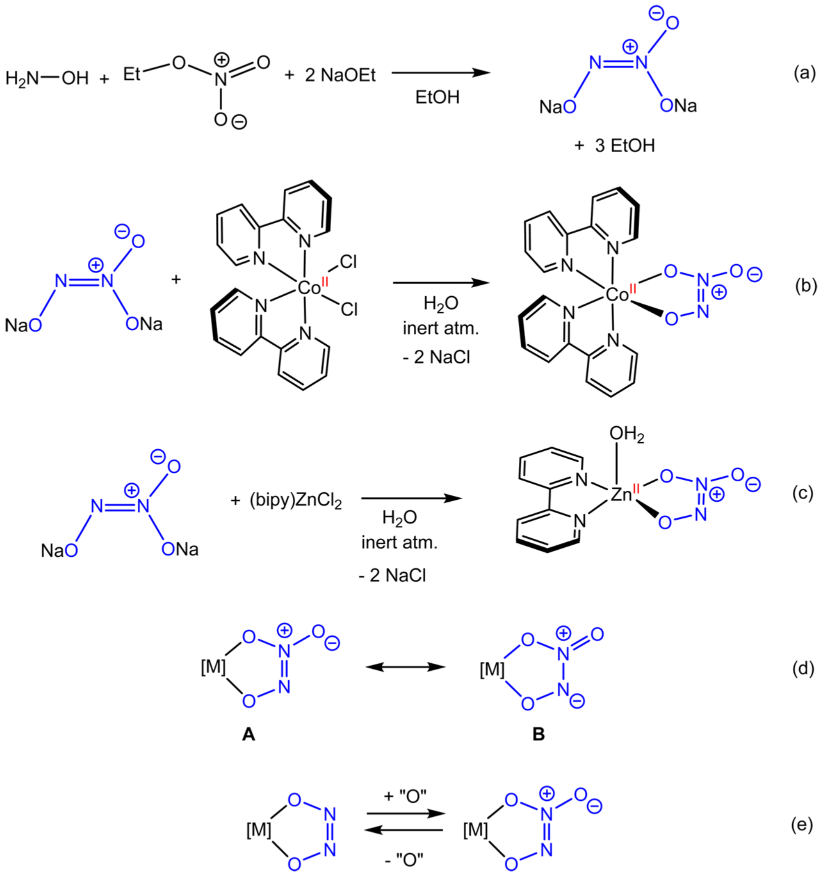
2.2.6. Chemistry of Oxohyponitrite. Any discussion of hyponitrite needs to include mention of the closely related oxohyponitrite, $[N_2O_3]^{2-}$, also known as the trioxodinitrate anion, α-oxohyponitrite, or Angeli's salt.[108,109] The chemistry of this anion is reasonably well established, and it is widely used as a HNO donor in in vitro studies.[110−113] It can be synthesized by the reaction of hydroxylamine with ethyl nitrate and sodium ethoxide (Scheme 18a),[43,111,114] a procedure that is similar to that reported for the synthesis of *trans*-$Na_2N_2O_2$ (Scheme 4a). Sodium trioxodinitrate can be isolated as its hydrate, $Na_2N_2O_3\cdot H_2O$,[114] which has been characterized by X-ray crystallography, but it can also be made in anhydrous form.[43] Curiously, its metal chemistry has not been widely explored, but there is some precedent for its ligation to a metal ion.[108] For example, the homoleptic trioxodinitrate complexes $[Co(NH_3)_6]_4[M(N_2O_3)_3]_3$ (M = Mn, Fe, Co, and Ni) have been reported,[115] but they have not been fully characterized. In addition, the mixed-ligand trioxodinitrate−bipyridine complexes (bipy)$Zn(N_2O_3)(H_2O)$ and $(bipy)_2Co(N_2O_3)$ have been prepared (Scheme 18). Both complexes have been structurally characterized, confirming their formulations. Interestingly, the N−N bond lengths for the Zn and Co derivatives are 1.280(5) and 1.333(11) Å, respectively. These values are slighly 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)$Zn(N_2O_3)(H_2O)$ and $(bipy)_2Co(N_2O_3)$ 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 N atom and a N−N single bond.[108]

Scheme 17. Synthesis of Cyclohexadienone Diazeniumdiolate and Its Use as a *cis*-Hyponitrite Synthon



DOI: 10.1021/acs.inorgchem.5b00516
Inorg. Chem. 2015, 54, 9330−9341

Scheme 18. Synthesis and Coordination Chemistry of an Oxohyponitrite Anion



In the greater context of *cis*-hyponitrite chemistry, the trioxodinitrate anion $[N_2O_3]^{2-}$ 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 O atom from $[N_2O_3]^{2-}$ would generate the *cis*-hyponitrite ligand. This could be achieved, for example, by reaction with an O atom acceptor such as Ph_3P (Scheme 18e).

3. SUMMARY AND OUTLOOK

The past decade has seen considerable improvement in our understanding of NO_x reduction, for both biological systems and heterogeneous catalysts. Several lines of evidence, including in situ catalyst monitoring, computational modeling, and coordination chemistry reactivity studies, point to the intermediacy of *cis*-hyponitrite in these reactions. However, there are still many unanswered questions with regard to hyponitrite reactivity because 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 hyponitrite complexes discussed in this review were formed by chance. Thus, the development of new hyponitrite synthons is of particular importance because this would allow for a systematic study of the hyponitrite reactivity. The development of earth-abundant catalysts for NO_x reduction is also of considerable interest. Most homogeneous catalysts employ noble metals;[116−118] however, with an improved knowledge of the hyponitrite reactivity, it may be possible to develop a homogeneous, 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 coligand that enforces 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 NOR and heterogeneous NO_x reduction catalysts.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Sloan Foundation and University of California Santa Barbara. T.W.H. is also grateful for International Short Visit funding from the Swiss National Science Foundation.

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