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Mechanistic Insights into the Formation of N_2O by a Nickel Nitrosyl Complex

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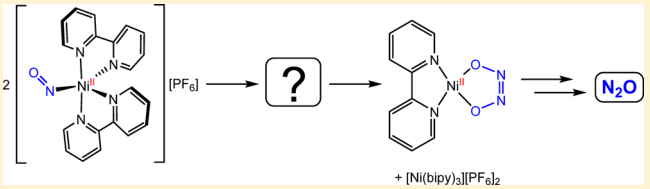
Supporting Information

ABSTRACT: Reaction of $[Ni(NO)(bipy)(Me_2phen)][PF_6]$ with 1 equiv of nitric oxide (NO) in CH_2Cl_2 results in the formation of N_2O and $[\{(Me_2phen)Ni(NO)\}_2(\mu-\eta^1\text{-}N:\eta^1\text{-}O)\text{-}NO_2)][PF_6]$ (**3**), along with the known complex, $[Ni(bipy)_3]\text{-}[PF_6]_2$ (**4**). The isolation of complex **3**, which contains a nitrite ligand, demonstrates that the reaction of $[Ni(NO)(bipy)\text{-}(Me_2phen)][PF_6]$ with exogenous NO results in NO disproportionation and not NO reduction. Complex **3** could also be accessed by reaction of $[Ni(NO)(Me_2phen)][PF_6]$ (**5**) with $(Me_2phen)Ni(NO)(NO_2)$ (**7**) in good yield. Complexes **3**, **5**, and **7** were fully characterized, including analysis by X-ray crystallography in the case of **3** and **7**. Furthermore, addition of 0.5 equiv of bipy to $[Ni(NO)(bipy)][PF_6]$ results in formation of the hyponitrite complex, $[\{(bipy)Ni(\kappa^2\text{-}O_2N_2)\}\eta^1\text{:}\eta^1\text{-}N,N\text{-}\{Ni(NO)(bipy)\}_2][PF_6]_2$ (**9**), in modest yield. Importantly, the hyponitrite ligand in **9** is thought to form via coupling of two NO^- ligands and not by coupling of a nucleophilic nitrosyl ligand (NO^-) with an electrophilic nitrosyl ligand (NO^+). X-ray crystallography reveals that complex **9** features a new binding mode of the *cis*-hyponitrite ligand.



INTRODUCTION

There is a widespread interest in understanding the mechanism of nitric oxide (NO) reduction,[1,2] especially in regards to the abatement of NO_x emissions from industrial and automotive point sources.[3,4] The direct transformation of NO to its constituent elements, N_2 and O_2, is thermodynamically favorable, but it is complicated by a high activation barrier.[5] An attractive alternative route is stepwise reduction, via an N_2O intermediate (e.g., $NO \rightarrow N_2O \rightarrow N_2$).[1,2,6] In this process, NO is reduced to N_2O by an external reductant, such as CO, H_2, or NH_3.[7−10] Metalloenzymes also perform the reduction of NO in a stepwise fashion; however, they employ proton and electron equivalents to generate N_2O, along with an equivalent of water.[2,11] This reaction is often thought to proceed via a hyponitrite ($N_2O_2^{2-}$) intermediate,[1,2] and in metalloenzymes, such as *NO reductase* (NOR) and *flavodiiron NO reductase* (FDP),[12−24] several different mechanisms have been suggested for the N−N bond-forming step, including a pathway that involves the coupling of two NO^- ligands.[11] In that regard, Lehnert and co-workers recently suggested that this so-called "super-reduced" mechanism is the most likely pathway for *flavodiiron NO reductase*.[25] This corroborates earlier work by the Collman and Karlin groups, who proposed similar mechanisms involving a reduced nitrosyl ligand.[13,15,16,19] A number of inorganic complexes have also been shown to perform the reduction of NO to N_2O and water.[26−31] For example, Trogler and co-workers investigated a Pd/Cu catalyzed reduction of NO.[26−28] In addition, a bimetallic ruthenium system has been shown to reduce NO, and, notably, the N_2O_2 intermediate in this process proved to be isolable.[1,30−33]

We recently reported the synthesis and characterization of a five-coordinate nickel nitrosyl complex, $[Ni(NO)(bipy)_2][PF_6]$ (**1**), which evolves N_2O when it stands in solution.[29] We considered a number of potential mechanisms for this process, which were inspired by those postulated for *NO reductase*.[11] These included the following: (**A**) coupling of two NO^- ligands via a bimetallic intermediate and (**B**) coupling of the NO^- ligand with NO gas (wherein homolysis of the Ni−NO bond is invoked to form the required equivalent of $NO^•$) (Scheme 1).[34] In our original report, we proposed that pathway **A** was most likely the operative pathway. This was supported by the differing reactivity of **1** and $[Ni(NO)(bipy)(Me_2phen)][PF_6]$ (**2**), as the latter does not generate N_2O on standing in solution. We suggested that the methyl groups on Me_2phen impart sufficient steric bulk about the Ni center in **2** to prevent a bimetallic coupling of the NO^- ligands from occurring. However, mechanism **B** was not ruled out completely, and herein we better evaluate this possibility. We also evaluate a third mechanism of NO reduction, namely, (**C**) coupling of an electrophilic NO^+ ligand with a nucleophilic NO^- ligand (Scheme 1). Precedent for this mechanistic pathway comes from the well-known ability of linear nitrosyl ligands to react with a wide variety of nucleophiles.[5,35−37] The classic example in this regard is $[Fe(CN)_5(NO)]^{2-}$, which reacts with many nucleophiles to give $[Fe(CN)_5(N(=O)L)]^{2-}$-type products.[35] Several other linear nitrosyl ligands exhibit electrophilic reactivity,[37,38] suggesting that electrophile/nucleophile coupling

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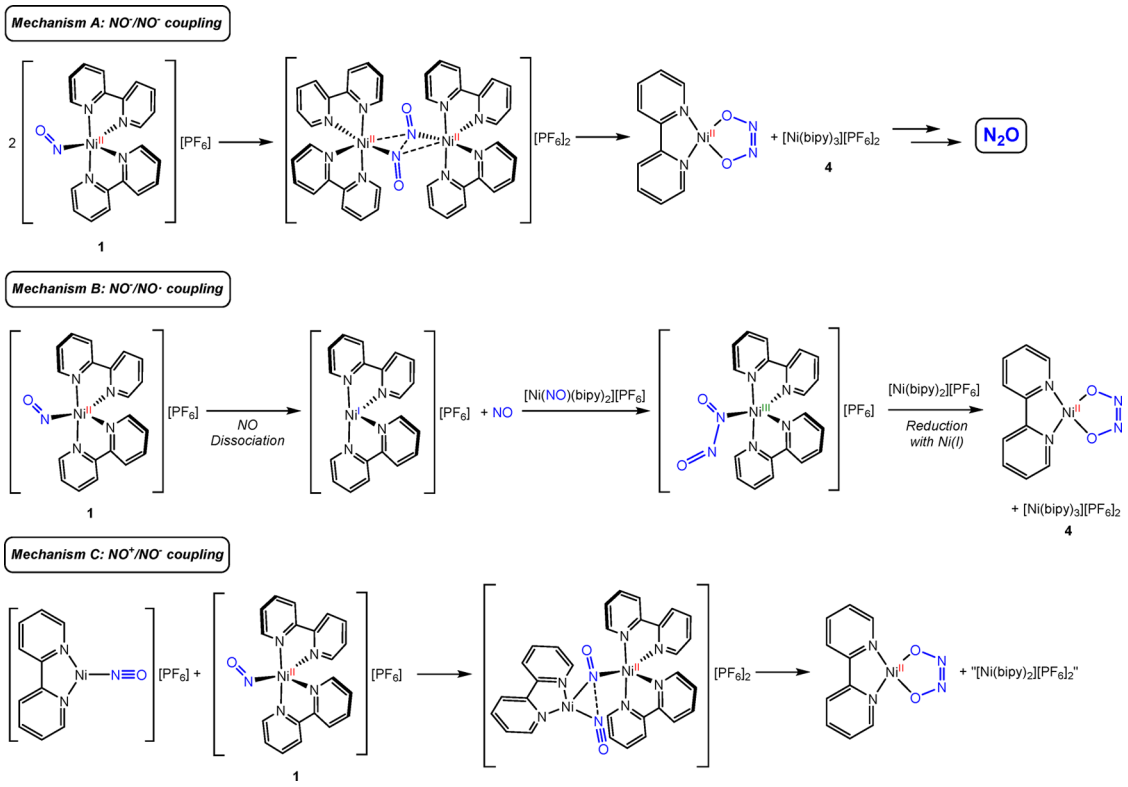
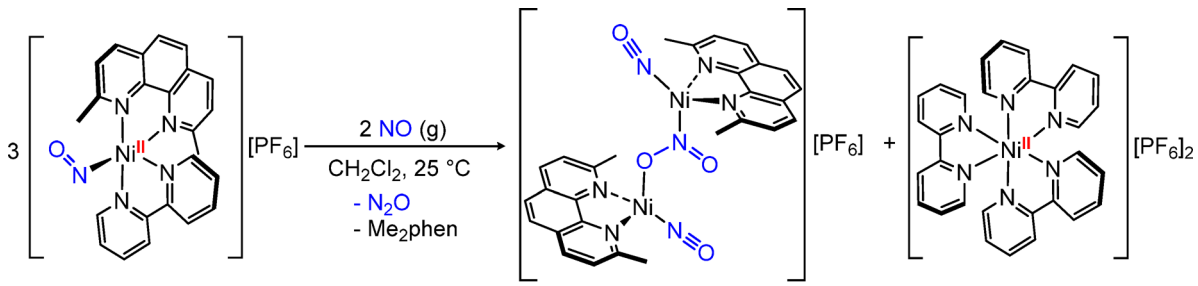
Scheme 1



Scheme 2



could also be operative in the formation of N_2O from complex **1**.

RESULTS AND DISCUSSION

NO Disproportionation Mediated by [Ni(NO)(bipy)(Me$_2$phen)][PF$_6$] (2). As previously reported, complex **1** reacts with exogenous NO gas to generate N_2O; however, identification of the other products formed during this transformation proved problematic, in part because of the complexity of the reaction mixture.[29] The complexity is likely derived from the competing NO reduction reaction, which is likely still operative even upon addition of exogenous NO. Despite this, we proposed that N_2O was mainly being formed by NO disproportionation, and not NO reduction, based on the predilection of M(NO$^-$) complexes to undergo electrophilic attack by NO(g) to yield NO disproportionation products.[39−41] To further evaluate this possibility, we explored the reactivity of the stable five-coordinate nickel nitrosyl complex, [Ni(NO)(bipy)(Me$_2$phen)][PF$_6$] (**2**) with exogenous NO, as this complex does not undergo the competing NO reduction reaction. Thus, treatment of a red solution of [Ni(NO)(bipy)(Me$_2$phen)][PF$_6$] (**2**) with 1 equiv of NO in CH_2Cl_2 results in a color change to blue-green over several hours (Scheme 2). The solution-phase IR spectrum of this mixture exhibits a vibration at 2223 cm^{-1}, which is assignable to the asymmetric stretch of N_2O.[41] After workup, a solid crystalline material consisting of two different crystal types was isolated. The separation of these two crystalline materials, one of which was dark blue and the other pale pink, was complicated by their similar solubility properties. Nonetheless, the partial characterization of the mixture was achieved. For instance, the ^{1}H NMR spectrum of the mixture reveals only two sets of polypyridyl resonances. One set of resonances, at 14.67, 46.57, and 63.18 ppm, is assignable to the previously characterized complex [Ni(bipy)$_3$][PF$_6$]$_2$ (**4**).[29] The second set of resonances, observed at 3.17, 7.70, and 8.26 ppm, in a 6:4:2 ratio, respectively, is assignable to [{(Me$_2$phen)Ni(NO)}$_2$(μ−η^1-*N*:η^1-*O*)-NO$_2$)][PF$_6$] (**3**). Importantly, there

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are no other major reaction products observed in the ^{1}H NMR spectrum (Figure S28). The dark blue/purple crystalline material was manually separated from the pale pink crystals. These crystals feature a ν_{NO} stretch at 1801 cm^{-1} in their IR spectrum, consistent with a nitrosyl ligand in a $NiL_2X(NO)$-type complex.[42] In addition, there are also vibrations at 1336, 1226, and 865 cm^{-1}, which are assignable to the asymmetric, symmetric, and bending modes, respectively, of a nitrito ligand.[43,44]

Complex **3** crystallizes in monoclinic space group *C*2/*c* and its solid-state molecular structure is illustrated in Figure 1.

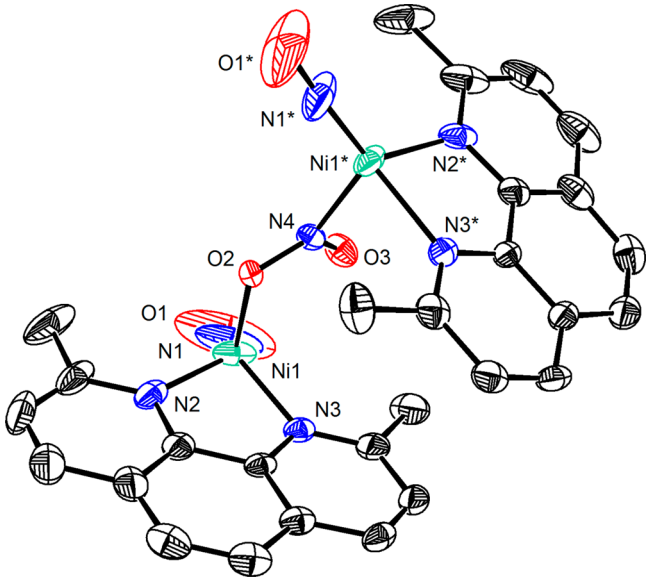


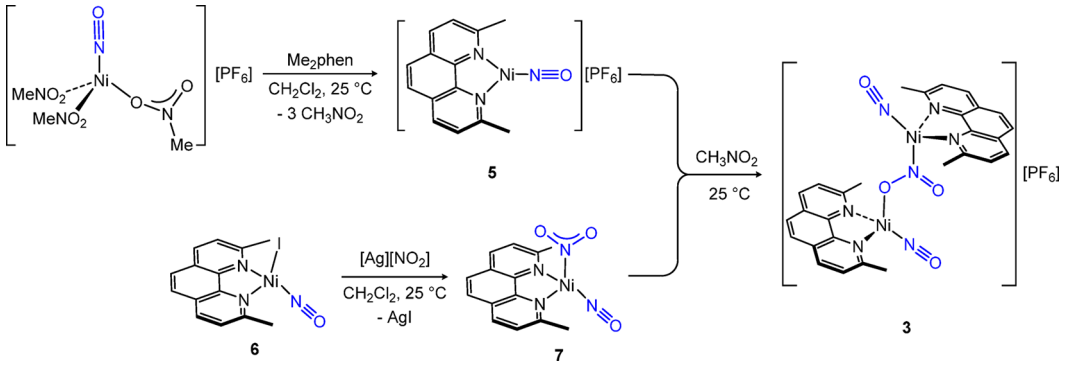
Figure 1. ORTEP drawing of [{(Me$_2$phen)Ni(NO)}$_2$(μ–η^1-*N*:η^1-*O*)-NO$_2$)][PF$_6$] (**3**) shown at 50% thermal ellipsoids. Hydrogen atoms, PF$_6$ anion, and the alternate position of the disordered NO$_2^-$ ligand have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ni1–N1 = 1.638(3), N1–O1 = 1.148(4), Ni1–N1–O1 = 177.1(3), Ni1–N2 = 2.009(3), Ni1–N3 = 2.021(2), Ni1–O2 = 2.075(8), N4–O2 = 1.239(7), N4–O3 = 1.225(9), N4–Ni1* = 2.024(11), O2–N4–O3 = 117.3(7).

Complex **3** features two Ni centers bridged by a nitrite ligand,[44] which adopts a μ–η^1:η^1-*N*,*O* binding mode.[45,46] It is situated on a crystallographically imposed C_2 rotation and is disordered over two positions in a 50:50 ratio. Each Ni center features a distorted tetrahedral coordination environment (τ_4 = 0.74),[47] consisting of a Me$_2$phen ligand, an NO ligand, and the aforementioned bridged nitrite ligand. The Ni–N(nitrite) and Ni–O(nitrite) bond lengths are Ni1–N4 = 2.024(11) Å and Ni1–O2 = 2.009(3) Å, respectively, and the nitrite N–O bond lengths are N4–O2 = 1.239(7) Å and N4–O3 = 1.225(9). In comparison, the Ni–N bond length for the closely related complex, (Me$_3$P)$_2$Ni(NO)(η^1-NO$_2$), is 1.997(6) Å,[48] whereas the N–O(nitrite) distances in [Ni(en)$_2$(μ–η^1:η^1-*N*,*O*-NO$_2$)-(BF$_4$)]$_n$ (en = ethylenediamine), which features an identical nitrite binding mode, are 1.27(2) and 1.22(2) Å.[49] Finally, the nitrosyl ligands in **3** exhibit metrical parameters typical of four-coordinate nickel nitrosyl complexes.[42,50−54] The large thermal ellipsoid observed for the oxygen atom of the nitrosyl ligand may be the result of unresolved positional disorder due to bending of the nitrosyl ligand. This is a relatively common phenomenon in metal nitrosyl complexes.[5]

Given the presence of both nitrite and N$_2$O in the reaction mixture, we suggest that complex **3** is formed as a result of a formal NO disproportionation (e.g., 3NO → NO$_2$ + N$_2$O).[55] Accordingly, we propose that the first step in the reaction sequence involves electrophilic attack by exogenous NO on the nitrosyl ligand of **2**, to generate an [N$_2$O$_2$]$^{n-}$-containing intermediate.[35,56−58] The [N$_2$O$_2$]$^{n-}$ ligand is subsequently attacked by a second equivalent of NO to give N$_2$O and the unobserved intermediate, [Ni(NO$_2$)(Me$_2$phen)(bipy)]-[PF$_6$].[56,57,59] This complex undergoes ligand exchange with a second equivalent of **2** to afford (Me$_2$phen)Ni(NO)(NO$_2$) and [Ni(bipy)$_2$(Me$_2$phen)]$^{2+}$. Further dipyridyl ligand scrambling yields [Ni(bipy)$_3$][PF$_6$]$_2$ (**4**), free Me$_2$phen, and the three-coordinate complex, [Ni(NO)(Me$_2$phen)]$^+$. The latter complex binds to the nitrite ligand in (Me$_2$phen)Ni(NO)(NO$_2$) to generate complex **3**. Notably, the extra steric bulk of the Me$_2$phen ligand, which inhibits N$_2$O formation by NO$^-$ coupling, does not inhibit the attack of the nitrosyl ligand by NO(g). Most importantly, the formation of **3** suggests that coupling of NO$^-$ and NO$^\bullet$ (reaction **B**) is not likely operative during nitrosyl ligand reduction in **1**, although it can clearly result in N$_2$O formation via disproportionation.

Metal-mediated NO disproportionation has been observed for a number of first row metal complexes, including those of Mn,[40,60,61] Fe,[41,62] Co,[39,63−66] and Cu.[57,59,67] For example, Tolman reported that addition of excess NO to Tp^{R}Cu (Tp^R = tris(1-pyrazolyl)hydroborate; R = Me or Ph) resulted in clean formation of Tp^{R}Cu(NO$_2$) and N$_2$O.[57,59] Similarly, Lippard and co-workers have reported the disproportionation of NO by a series of Mn and Fe tropocoronand complexes,[40,41] while Caulton and co-workers reported the disproportionation of NO by [Co(NO)(en)$_2$(L)]$^{2+}$ (L = MeOH).[39] Significantly, in these

Scheme 3



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examples NO disproportionation is proposed to proceed via reaction of exogenous NO with a reduced NO^- ligand, similar to that suggested for complex **2**.[40,41]

Independent Synthesis of [{(Me$_2$phen)Ni(NO)}$_2$(μ–η^1-*N*:η^1-*O*)-NO$_2$)][PF$_6$]. To complete the characterization of complex **3**, we sought an independent route for its synthesis. According to the mechanism described above, the generation of complex **3** should be achievable by reaction of [Ni(NO)-(Me$_2$phen)][PF$_6$] with (Me$_2$phen)Ni(NO)(NO$_2$). Thus, addition of Me$_2$phen to a CH_2Cl_2 solution of [Ni(NO)-(CH$_3$NO$_2$)$_3$][PF$_6$][42] affords [Ni(NO)(Me$_2$phen)][PF$_6$] (**5**), which can be isolated as a green microcrystalline solid in 83% yield (Scheme 3). Its IR spectrum in CH_2Cl_2 exhibits an NO stretch at 1861 cm^{-1}, which is slightly lower than the corresponding NO stretch in [Ni(NO)(bipy)][PF$_6$] (1868 cm^{-1}),[29] revealing the stronger donor ability of Me$_2$phen. Finally, the ^{1}H NMR spectrum of **5** contains four resonances at 3.88, 7.81, 8.04, and 8.44 ppm in a 6:2:2:2 ratio, respectively, consistent with the presence of the Me$_2$phen ligand.

Addition of Me$_2$phen to a THF solution of Ni(NO)I(THF)$_n$ affords (Me$_2$phen)Ni(NO)(I) (**6**), which can be isolated as a green powder in 79% yield (based on Me$_2$phen). Subsequent reaction of **6** with $AgNO_2$ yields (Me$_2$phen)Ni(NO)(NO$_2$) (**7**), which can be isolated as an blue-green microcrystalline solid in 47% yield (Scheme 3). Its solid-state IR spectrum (Nujol mull) features an ν_{NO} stretch at 1798 cm^{-1}, along with vibrations at 1336 (asym), 1321 (sym), and 872 (bend) cm^{-1}, assignable to the three expected modes of an N-bound nitrite ligand.[44] In addition, the ^{1}H NMR spectrum of **7** contains four sharp resonances in a 6:2:2:2 ratio, consistent with the presence of the Me$_2$phen ligand.

A crystal of **7** suitable for X-ray diffraction was grown from a dilute CH_2Cl_2 solution at −25 °C. Its solid-state molecular structure is shown in Figure 2. In the solid-state, the nickel center is bound by a Me$_2$phen ligand, an NO ligand, and an N-bound nitrite ligand, in a pseudotetrahedral coordination environment (τ_4 = 0.72).[47] As predicted by IR spectroscopy, the nitrite ligand binds to the Ni center through the N atom

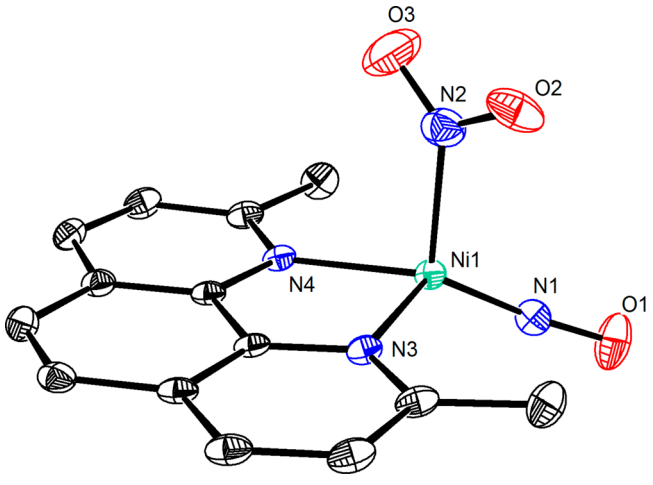

Figure 2. ORTEP drawing of (Me$_2$phen)Ni(NO)(NO$_2$) (**7**) shown at 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ni1–N1 = 1.641(2), Ni1–N2 = 1.979(3), Ni1–N3 = 2.017(2), Ni1–N4 = 2.025(3), N1–O1 = 1.164(3), N2–O2 = 1.256(3), N2–O3 = 1.209(4), Ni1–N1–O1 = 168.4(2), Ni1–N2–O2 = 117.7(2), Ni1–N2–O3 = 122.8(2).

and features Ni–N (Ni1–N2 = 1.979(3) Å) and N–O bond lengths (N2–O2 = 1.256(3) and N2–O3 = 1.209(4) Å) similar to those observed in the closely related complex, (Me$_3$P)$_2$Ni(NO)(η^1-NO_2).[48] The metrical parameters of the nitrosyl ligand in **7** (Ni1–N1 = 1.641(2) Å, N1–O1 = 1.164(3) Å, Ni1–N1–O1 = 168.4(2)°) are consistent with other four-coordinate nickel nitrosyl complexes.[42,68,69] For comparison, the nitrosyl Ni–N and N–O bond lengths in (Me$_3$P)$_2$Ni(NO)(η^1-NO_2) are 1.648(6) and 1.177(7) Å, respectively.[48]

Addition of a CH_3NO_2 solution of [Ni(NO)(Me$_2$phen)]-[PF$_6$] (**5**) to a CH_2Cl_2 slurry of (Me$_2$phen)Ni(NO)(NO$_2$) (**7**) results in a color change to royal blue. Storage of this solution at −25 °C results in the precipitation of **3** as a dark blue/purple crystalline solid in 55% isolated yield. Complex **3** is insoluble in hexanes, Et_2O, and CH_2Cl_2 and only exhibits modest solubility in highly polar solvents, such as CH_3NO_2 and MeCN. The ^{1}H NMR spectrum of **3** in CD_3NO_2 exhibits four resonances at 3.42, 7.74, 7.75, and 8.29 ppm, in a 12:4:4:4 ratio, respectively, assignable to the protons of Me$_2$phen ligands. Notably, only one Me$_2$phen environment is observed in solution, suggesting rapid exchange of the bridged nitrite ligand.

NO Reduction Mediated by [Ni(NO)(bipy)$_2$][PF$_6$] (1). We also explored the possibility that NO reduction could occur by coupling of the nucleophilic NO^- ligand in **1** with an electrophilic, linear NO^+ ligand (Reaction **C**). Importantly, the NO^+/NO^- coupling pathway was considered a viable pathway because of the observed lability of the bipyridine ligands in **1**. In particular, we found that addition of triphenylphosphine (PPh_3) to complex **1** in CH_2Cl_2 results in a rapid reaction to generate a deep purple solution. Monitoring the reaction by solution IR spectroscopy reveals formation of a new ν(NO) absorption at 1793 cm^{-1}, assignable to [Ni(NO)(bipy)(PPh$_3$)][PF$_6$] (**8**) (Scheme 4). On a preparative scale, PPh_3 reacts with [Ni(NO)(bipy)][PF$_6$] in CH_2Cl_2 to generate a purple solution, from which complex **8** can be isolated in 60% yield. The full characterization data of **8** is presented in the Supporting Information. The facile exchange of a bipy ligand for PPh_3 suggests that [Ni(NO)(bipy)][PF$_6$], which features a linear NO^+ ligand, could be accessed in situ via dissociation of a bipy ligand in **1**.

To test the viability of pathway **C**, a CH_2Cl_2 solution of [Ni(NO)(bipy)][PF$_6$] was treated with 0.5 equiv of bipy, which conveniently generates a 1:1 mixture of [Ni(NO)-(bipy)][PF$_6$] and [Ni(NO)(bipy)$_2$][PF$_6$] (**1**), in situ. Upon addition of 0.5 equiv of bipy to [Ni(NO)(bipy)][PF$_6$], the dark green solution initially turns red-brown. Over the course of 30 min, a dark blue crystalline solid, which was determined to be [{(bipy)Ni(κ^2-O_2N_2)}η^1:η^1-*N*,*N*-{Ni(NO)(bipy)}$_2$][PF$_6$]$_2$ (**9**), precipitates from the reaction mixture in 43% yield (Scheme 4). Analysis of the supernatant by ^{1}H NMR spectroscopy reveals the presence of [Ni(bipy)$_3$][PF$_6$]$_2$ (**4**) in the reaction mixture (Figure S31).[29] Also formed in the reaction is an unidentified [Ni(NO)(bipy)(L)]$^+$-type complex, as revealed by resonances at 7.93, 8.08, 8.13, and 10.17 ppm in the ^{1}H NMR spectrum of the reaction mixture, which may account for the moderate isolated yield of complex **9**.

The ^{1}H NMR spectrum of **9** in CD_3NO_2 exhibits eight sharp resonances in the diamagnetic region, assignable to two different bipy ligand environments, in a 2:1 ratio. The more intense set of resonances at 8.02, 8.29, 8.32, and 10.35 ppm are assignable to the aryl CH bipy protons in the [Ni(NO)(bipy)]$^+$ fragment. The second set of resonances at 7.29, 7.41, 7.99, and

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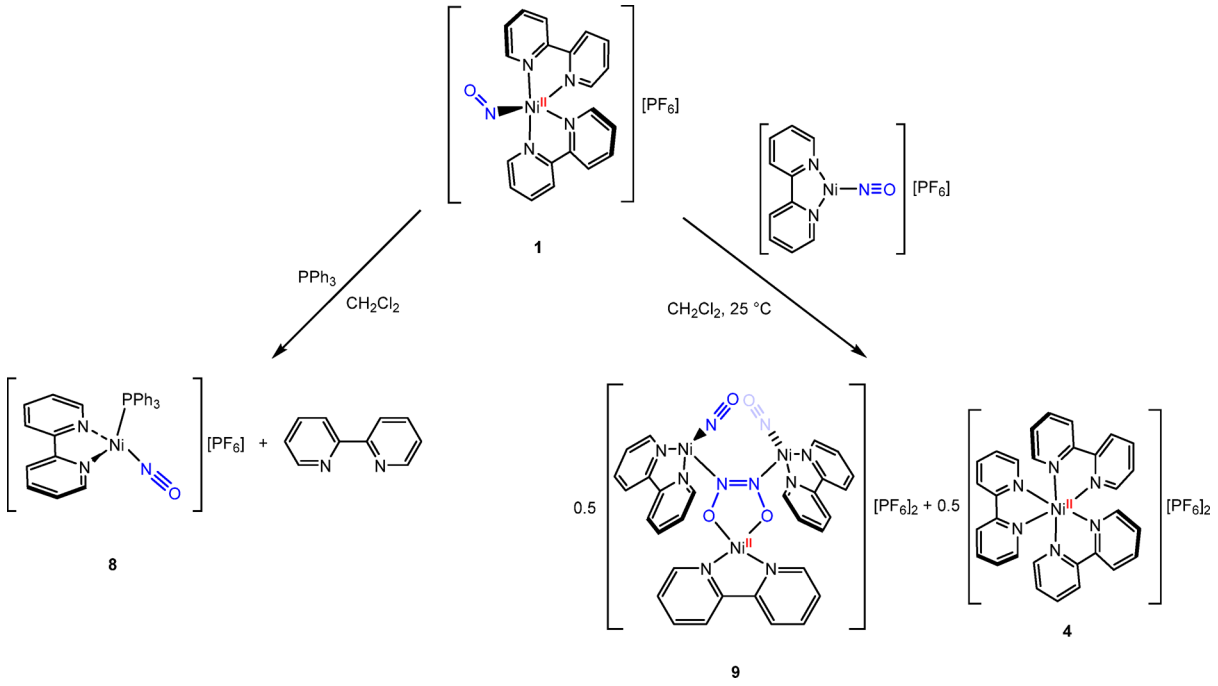
Scheme 4



8.10 ppm closely match those observed for (bipy)Ni(κ^2-O_2N_2).[29] Finally, its ^{19}F NMR spectrum in CD_3NO_2 features a sharp doublet at −73.27 ppm, assignable to the PF_6 anion. Complex **9** is soluble in CH_3NO_2 but insoluble in hexanes or CH_2Cl_2.

Complex **9** crystallizes in the triclinic space group $P\bar{1}$, and its solid-state molecular structure is shown in Figure 3. The asymmetric unit contains two independent molecules of **9**, but only one will be discussed in detail. The cationic portion of complex **9** contains a *cis*-hyponitrite ligand coordinated to a [(bipy)Ni]$^{2+}$ fragment in a κ^2 fashion via the two oxygen atoms. In addition, the N atoms of the $[N_2O_2]^{2-}$ moiety are each capped by a [Ni(NO)(bipy)]$^+$ fragment.[33,70] The metrical parameters of the $[N_2O_2]^{2-}$ group (N11−O5 = 1.366(11) Å, N12−O6 = 1.377(12) Å, N11−N12 = 1.279(13) Å) are similar to those previously reported for group 10 $[N_2O_2]^{2-}$ complexes.[29,32,33,71] Notably, there is only a minor perturbation of the $[N_2O_2]^{2-}$ metrical parameters upon coordination to the [Ni(NO)(bipy)]$^+$ fragment, relative to the parent molecule (bipy)Ni(κ^2-O_2N_2).[29] The metrical parameters of the two nitrosyl ligands in **9** are consistent with those observed in other [Ni(NO)(bipy)L]$^+$-type complexes, while the geometries about the Ni(NO) centers are distorted tetrahedral, as revealed by the τ_4 values of 0.74 and 0.75.[47]

Interestingly, the κ^4 binding mode of the hyponitrite ligand in **9** is a new binding mode for this ligand.[33] For comparison, the only other example of a hyponitrite with a κ^4 binding mode is $Co_4(NO)_8(NO_2)_2$(*trans*-N_2O_2).[72] However, in this example, the hyponitrite ligand is in the *trans* configuration and binds to four different Co centers.[72] Importantly, the binding of the Lewis acidic [Ni(NO)(bipy)]$^+$ fragment to the nitrogen atom in $[N_2O_2]^{2-}$ reveals the nucleophilic nature of the *cis*-hyponitrite ligand in (bipy)Ni(κ^2-O_2N_2). Structurally characterized examples of the *cis*-hyponitrite ligand are relatively rare. As a result, its chemistry is not well understood, making any new insight into its behavior potentially useful. In particular, the recognition of its nucleophilic nature may have consequences

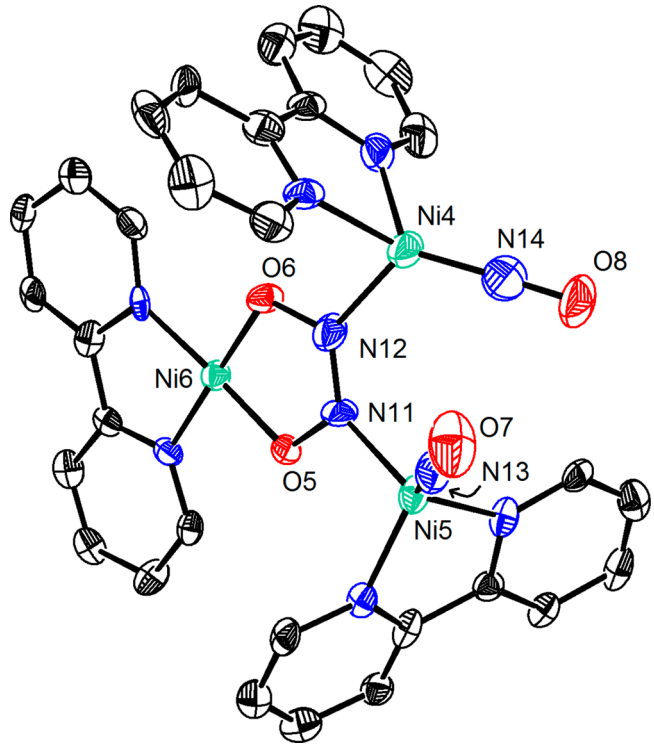


Figure 3. ORTEP drawing of [{(bipy)Ni(κ^2-O_2N_2)}η^1:η^1-*N*,*N*-{Ni(NO)(bipy)}$_2$][PF_6]$_2$ (**9**) shown at 50% thermal ellipsoids. Only one of the independent molecules in the asymmetric cell is shown. The hydrogen atoms, two PF_6 anions, and one CH_2Cl_2 solvent molecule have been excluded for clarity. Selected bond lengths (Å) and bond angles (deg): Ni4−N14 = 1.628(11), N14−O8 = 1.164(12), Ni4−N12 = 2.017(10), Ni5−N13 = 1.627(11), N13−O7 = 1.166(13), Ni5−N11 = 2.036(10), Ni6−O5 = 1.806(7), Ni6−O6 = 1.802(7), O5−N11 = 1.366(11), O6−N12 = 1.377(12), N11−N12 = 1.279(13), Ni4−N14−O8 = 175.4(11), Ni5−N13−O7 = 171.6(11).

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for our understanding of the mechanisms of NO reduction in metalloenzymes.[32,33]

We suggest that complex **9** is generated as a result of the previously described NO reduction mediated by $[Ni(NO)(bipy)_2][PF_6]$,[29] which generates $(bipy)Ni(\kappa^2\text{-}O_2N_2)$ and $[Ni(bipy)_3][PF_6]_2$ (**4**). Subsequently, $(bipy)Ni(\kappa^2\text{-}O_2N_2)$ is trapped by two equiv of $[Ni(NO)(bipy)][PF_6]$ to afford complex **9**, which precipitates from the reaction mixture because of its insolubility in CH_2Cl_2. According to this mechanistic sequence, it is the NO^- ligands of **1** that are transformed into the $[N_2O_2]^{2-}$ ligand, whereas the linear NO nitrosyl ligands of $[Ni(NO)(bipy)]^+$ fragment remain intact, suggesting that the NO^+/NO^- coupling reaction (pathway **C**) is not operative in the N−N bond forming process.

SUMMARY

In this report, we have investigated the plausibility of two different mechanistic pathways for the formation of N_2O from the coupling of the nitrosyl ligands in $[Ni(NO)(bipy)_2][PF_6]$, namely, coupling of NO^- with exogenous NO gas, or the coupling of NO^- with an electrophilic linear NO^+ ligand. To investigate the potential viability of the $NO^-/NO^\bullet$ pathway, $[Ni(NO)(bipy)(Me_2phen)][PF_6]$, a complex that is not susceptible to reductive NO coupling, was reacted with 1 equiv of exogenous NO. This afforded $[Ni(bipy)_3][PF_6]_2$, along with N_2O and $[\{(Me_2phen)Ni(NO)\}_2(\mu\text{-}\eta^1\text{-}N{:}\eta^1\text{-}O)\text{-}NO_2)][PF_6]$ (**3**), which are the products of NO disproportionation. This result suggests that NO gas is not involved in the formation of N_2O mediated by $[Ni(NO)(bipy)_2][PF_6]$, as the products of NO disproportionation are not detected in this transformation. This is perhaps not surprising, as the Ni−NO bond homolysis required to generate free NO gas is likely a high energy process. In addition, it should be operative in both complexes **1** and **2**, given their electronic similarity, yet complex **2** is stable with respect to loss of N_2O. To evaluate the viability of N−N bond formation via coupling of a nucleophilic nitrosyl ligand (NO^-) with an electrophilic nitrosyl ligand (NO^+), we explored the reaction of $[Ni(NO)(bipy)_2][PF_6]$ with $[Ni(NO)(bipy)][PF_6]$. This resulted in the isolation of $[\{(bipy)Ni(\kappa^2\text{-}O_2N_2)\}\eta^1{:}\eta^1\text{-}N,N\text{-}\{Ni(NO)(bipy)\}_2][PF_6]_2$, a trimetallic nickel complex that features the hyponitrite fragment, $(bipy)Ni(\kappa^2\text{-}O_2N_2)$, capped by two $[Ni(NO)(bipy)]^+$ moieties. While we do observe the products of NO reduction in this reaction (i.e., the hyponitrite ligand), we believe they are derived from the previously described coupling of two NO^- ligands and not coupling of an NO^- ligand with an NO^+ ligand. Overall, the results presented in this report have not demonstrated the viability of any alternate coupling mechanisms, and thus we still favor the previously proposed NO^-/NO^- coupling mechanism for construction of the N−N bond in this system.

EXPERIMENTAL SECTION

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Nitromethane was recrystallized from Et_2O three times and then distilled over $MgSO_4$ or CaH_2. Dichloromethane was degassed and stored over 3 Å sieves for 24 h before use. 2,9-Dimethylphenanthroline was purchased from Sigma-Aldrich and recrystallized from toluene at −25 °C. Diethyl ether, hexane, THF, and toluene were dried using a Vacuum Atmospheres DRI-SOLV solvent purification system. CD_2Cl_2 and CD_3NO_2 were dried over activated 3 Å molecular sieves for 24 h prior to use. Nitrogen monoxide gas was purchased from Praxair, and NO_2 was removed by passing the gas through a spiral silica column cooled to −78 °C. $[Ni(CH_3NO_2)_3(NO)][PF_6]$,[42] $[Ni(NO)(bipy)(Me_2phen)][PF_6]$,[29] and $Ni(NO)(I)(THF)_n$[73] were synthesized using previously published methods. All other reagents were purchased from commercial suppliers and used as received.

NMR spectra were recorded on a Varian UNITY INOVA 400 or Varian UNITY INOVA 500 spectrometer. ^1H and ^{13}C NMR spectra were referenced to external $SiMe_4$ (δ = 0) using the residual protio solvent peaks as an internal standard (^1H NMR experiments: δ 5.32 for CH_2Cl_2, 1.32 for CH_3CN, and 4.32 for CH_3NO_2; ^{13}C NMR experiments: δ 53.83 for CH_2Cl_2). $^{19}F\{^1H\}$ NMR spectra were referenced to external $CFCl_3$, and $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. IR spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer using NaCl salt plates for Nujol mulls or CaF_2 plates for solution-phase experiments. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Synthesis of $[\{(Me_2phen)Ni(NO)\}_2(\mu\text{-}\eta^1\text{-}N{:}\eta^1\text{-}O)\text{-}NO_2)][PF_6]$ (3). A 4 mL scintillation vial was charged with a CH_2Cl_2 (0.5 mL) solution of $[Ni(NO)(Me_2phen)(bipy)][PF_6]$ (27 mg, 0.044 mmol). This vial was placed, uncapped, into a 20 mL scintillation vial containing a CH_2Cl_2 solution of $[Ni(NO)(bipy)][PF_6]$ (28 mg, 0.072 mmol) and 10 drops of THF. Excess TEMPO (31 mg, 0.20 mmol) was added to the outer vial as a CH_2Cl_2 solution (1 mL), which generated NO(g);[34] the vial was quickly capped and placed in a freezer set to −25 °C. Storage of this two-vial system for 24 h resulted in the deposition of dark blue blocks (2.4 mg, 10% yield), which were identified as $[\{(Me_2phen)Ni(NO)\}_2(\mu\text{-}\eta^1\text{-}N{:}\eta^1\text{-}O)\text{-}NO_2)][PF_6]$ by X-ray crystallography.

Large Scale Synthesis of $[\{(Me_2phen)Ni(NO)\}_2(\mu\text{-}\eta^1\text{-}N{:}\eta^1\text{-}O)\text{-}NO_2)][PF_6]$ (3). A 20 mL scintillation vial was charged with $[Ni(NO)(bipy)(Me_2phen)][PF_6]$ (115 mg, 0.192 mmol) and CH_2Cl_2 (2 mL). Using a gastight syringe, a portion (5 mL) of the head space was removed and then backfilled with NO gas (1 atm, 4.7 mL, 0.193 mmol). The reaction was left to stand at room temperature for 72 h, during which time the solvent had evaporated, leaving a mixture of two materials with different crystal morphologies. The solid was washed with hexanes (5 mL) and then dried in vacuo to give a blue powder with a total mass of 76 mg. The ^1H NMR spectrum of this solid revealed the presence of $[Ni(bipy)_3][PF_6]_2$ (**4**) and $[\{(Me_2phen)Ni(NO)\}_2(\mu\text{-}\eta^1\text{-}N{:}\eta^1\text{-}O)\text{-}NO_2)][PF_6]$ (**3**). ^1H NMR (CD_3NO_2, 400 MHz, 22 °C): δ 3.17 (br s, 6H, Me), 7.70 (br s, 4H, aryl CH Me_2phen), 8.26 (br s, 2H, aryl CH Me_2phen), 14.67 (br s, bipy CH, $[Ni(bipy)_3][PF_6]_2$), 46.57 (br s, bipy CH, $[Ni(bipy)_3][PF_6]_2$), 63.18 (br s, bipy CH, $[Ni(bipy)_3][PF_6]_2$). ^{31}P NMR (CD_3NO_2, 162 MHz, 22 °C): δ −144.80 (sept, PF_6, J_{P-F} = 708 Hz). ^{19}F NMR (CD_3NO_2, 376 MHz, 22 °C): δ −73.6 (d, PF_6^-, J_{P-F} = 703 Hz). The presence of $[Ni(bipy)_3][PF_6]_2$ was further confirmed by a unit cell determination of a pale pink crystal: a = 18.31 Å, b = 18.31 Å, c = 16.45; α = 90, β = 90, γ = 120. These parameters match the previously reported unit cell for $[Ni(bipy)_3][PF_6]_2$.[74] The presence of $[\{(Me_2phen)Ni(NO)\}_2(\mu\text{-}\eta^1\text{-}N{:}\eta^1\text{-}O)\text{-}NO_2)][PF_6]$ was also confirmed by a unit cell determination on a blue crystal: a = 14.76 Å, b = 12.98 Å, c = 16.49; α = 90, β = 108.88, γ = 90, which matches the unit cell of complex **3**.

$[Ni(NO)(Me_2phen)][PF_6]$ (5). To a CH_2Cl_2 solution (3 mL) of $[Ni(NO)(CH_3NO_2)_3][PF_6]$ (166 mg, 0.397 mmol) was added a CH_2Cl_2 solution (2 mL) of 2,9-dimethylphenanthroline (82 mg, 0.39 mmol). A green microcrystalline precipitate formed immediately. After storage of this solution at −25 °C for 1 h, the solution was decanted, and the solid was dried in vacuo (92 mg, 53% yield). Anal. Calcd for $C_{14}H_{12}F_6N_3NiOP$: C, 38.05; H, 2.74 N, 9.51. Found: C, 38.08; H, 2.38; N, 9.18. ^1H NMR (CD_2Cl_2, 400 MHz, 22 °C): δ 3.88 (s, 6H, Me), 7.81 (s, 2H, aryl H), 8.04 (d, 2H, aryl H, J_{HH} = 8 Hz), 8.44 (d, 2H, aryl H, J_{HH} = 8 Hz). ^{31}P NMR (CD_2Cl_2, 162 MHz, 22 °C): δ −144.42 (sept, PF_6, J_{P-F} = 710 Hz). ^{19}F NMR (CD_2Cl_2, 376 MHz, 22 °C): −73.84 ppm (d, PF_6, J_{P-F} = 711 Hz). ^1H NMR (CD_3CN, 400 MHz, 22 °C): δ 3.76 (s, 6H, Me), 7.99 (s, 2H, aryl H), 8.13 (d, 2H, aryl H, J_{HH} = 8 Hz), 8.61 (d, 2H, aryl H, J_{HH} = 8 Hz). IR (Nujol mull, cm^{-1}): 1881 (s, ν_{NO}). IR (CH_2Cl_2, cm^{-1}): 1861 (s, ν_{NO}).

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Table 1. X-ray Crystallographic Data for Complexes 3, 7, and 9

	3	7	9·0.5CH_2Cl_2
empirical formula	$C_{28}H_{24}F_6N_7Ni_2O_4P$	$C_{14}H_{12}N_4NiO_3$	$C_{30.5}H_{24}ClF_{12}N_{10}Ni_3O_4P_2$
cryst habit, color	cube, dark blue	brick, blue	needle, blue
cryst size (mm)	0.12 × 0.10 × 0.10	0.31 × 0.15 × 0.05	0.16 × 0.12 × 0.10
cryst syst	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$
vol ($Å^3$)	3002.39(14)	1379.38(15)	3961.3(19)
a (Å)	14.8203(4)	10.6523(6)	10.837(3)
b (Å)	12.9170(3)	12.1166(8)	16.351(5)
c (Å)	16.6160(5)	11.3286(8)	23.731(6)
α (deg)	90	90	70.639(7)
β (deg)	109.204(2)	109.374(5)	88.309(7)
γ (deg)	90	90	86.922(6)
Z	4	4	4
fw (g/mol)	784.93	342.99	2192.23
density (calcd) (Mg/m^3)	1.736	1.652	1.838
abs coeff (mm^{-1})	1.394	1.425	1.668
F_{000}	1592	704	2192
total no. reflns	13098	7920	23403
unique reflns	3737	2805	13190
R_{int}	0.0261	0.0364	0.0851
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0458, wR_2 = 0.1057	R_1 = 0.0357, wR_2 = 0.0837	R_1 = 0.0982, wR_2 = 0.2573
largest diff peak and hole ($e^-Å^{-3}$)	0.732 and −1.174	1.043 and −0.434	2.108 and −1.865
GOF	1.132	1.028	1.227

(Me_2phen)Ni(NO)(I) (6). To a THF solution (4 mL) of Me_2phen (231 mg, 1.11 mmol) was added a THF solution (5 mL) of Ni(NO)(I)$(THF)_n$ (279 mg). A green crystalline solid began to precipitate immediately from the solution. The reaction mixture was stirred for 30 min, whereupon the solution was decanted from the solid. The solid was dried in vacuo for 1 h to yield a green microcrystalline product (370 mg, 79% yield, based on Me_2phen). Anal. Calcd for $C_{14}H_{12}IN_3NiO$: C, 39.67; H, 2.85; N, 9.91. Found: C, 39.61; H, 2.46; N, 9.60. ^{1}H NMR (CD_2Cl_2, 400 MHz, 22 °C): δ 3.88 (s, 6H, Me), 7.80 (s, 2H, aryl-H), 7.93 (d, 2H, aryl H, J_{HH} = 8 Hz), 8.35 (d, 2H, aryl H, J_{HH} = 8 Hz). ^{13}C NMR (CD_2Cl_2, 125 MHz, 22 °C): δ 28.7, 126.1, 126.5, 127.8, 137.9, 143.6, 163.4. IR (CH_2Cl_2, cm^{-1}): 1788 (s, ν_{NO}). IR (Nujol mull, cm^{-1}): 1793(s, ν_{NO}).

(Me_2phen)Ni(NO)(NO_2) (7). To a suspension of (Me_2phen)Ni(NO)(I) (196 mg, 0.46 mmol) in CH_2Cl_2 (7 mL) was added $AgNO_2$ (75 mg, 0.49 mmol). The solution immediately changed color from green to deep blue, concomitant with the formation of a white precipitate. The reaction mixture was stirred for 45 min, whereupon the solution was filtered through a Celite plug (2 cm × 0.5 cm) supported on glass wool. The solution was then concentrated to 4 mL in vacuo and layered with hexanes (5 mL). Subsequent storage at −25 °C for 24 h resulted in the deposition of an indigo solid (110 mg). This solid was redissolved in CH_2Cl_2 (1 mL), and the solution was then layered with hexane (3 mL). Storage of this solution at −25 °C for 24 h resulted in the deposition of analytically pure indigo microcrystalline solid (74 mg, 47% yield). Anal. Calcd for $C_{14}H_{12}N_4NiO_3$: C, 49.03; H, 3.53; N, 16.34. Found: C, 48.82; H, 3.32; N, 16.16. ^{1}H NMR (CD_2Cl_2, 400 MHz, 22 °C): δ 3.85 (s, 6H, Me), 7.83 (s, 2H, aryl-H), 7.98 (d, 2H, aryl-H, J_{HH} = 8 Hz), 8.39 (d, 2H, aryl-H, J_{HH} = 8 Hz). ^{13}C NMR (CD_2Cl_2, 125 MHz, 22 °C): δ 28.19 (Me), 126.1, 126.9, 127.9, 138.2. The quaternary carbon of the Me_2phen ligand was not observed. IR (CH_2Cl_2, cm^{-1}): 1792 (s, ν_{NO}). IR (Nujol mull, cm^{-1}): 1798 (s, ν_{NO}), 1621 (w), 1587 (m), 1567 (m), 1372 (m), 1336 (s, ν_{asym} NO_2), 1321 (s, ν_{sym} NO_2), 1229 (m), 1150 (m) 1036 (w), 940 (w), 872 (m, ν_{bend} NO_2), 843 (w), 806 (w), 784 (w), 660 (w).

Independent Synthesis of [{(Me_2phen)Ni(NO)}$_2$(μ−η^1-*N*:η^1-*O*)-NO_2)][PF_6] (3). In a 20 mL scintillation vial, a CH_3NO_2 solution (1 mL) of [Ni(NO)(Me_2phen)][PF_6] (70 mg, 0.16 mmol) was layered onto a slurry of (Me_2phen)Ni(NO)(NO_2) (51 mg, 0.15 mmol) in CH_2Cl_2 (3 mL). This resulted in the formation of a clear blue solution. Subsequent storage of the vial at −25 °C for 16 h resulted in the deposition of indigo blocks. The supernatant was then decanted, and the solid was washed with CH_2Cl_2 (2 × 1 mL) and then dried in vacuo (65 mg, 55% yield). Anal. Calcd for $C_{28}H_{24}F_6N_7Ni_2O_4P$: C, 42.85; H, 3.08; N, 12.49. Found: C, 42.48; H, 2.79; N, 12.75. ^{1}H NMR (CD_3NO_2, 400 MHz, 22 °C): δ 3.42 (s, 6H, Me), 7.74 (s, 2H, aryl H), 7.75 (d, 2H, aryl H, J_{HH} = 8 Hz), 8.29 (d, 2H, aryl H, J_{HH} = 8 Hz). ^{31}P NMR (CD_2Cl_2, 163 MHz, 22 °C): δ −144.80 (sept, PF_6, J_{P-F} = 710 Hz). ^{19}F NMR (CD_2Cl_2, 376 MHz, 22 °C): −73.61 ppm (d, PF_6, J_{P-F} = 703 Hz). IR (Nujol mull, cm^{-1}): 1801 (s, ν_{NO}), 1591 (w), 1568 (w), 1509 (w), 1427 (w), 1336 (m, ν_{asym} NO_2), 1226 (m, ν_{sym} NO_2), 1152 (w), 1106 (vw), 1022 (w), 865 (s, ν_{bend} NO_2), 841 (s, PF_6), 815 (w), 785 (w), 681 (w), 660 (w), 557 (m).

[{(bipy)Ni(κ^2-O_2N_2)}η^1:η^1-*N*,*N*-{Ni(NO)(bipy)}$_2$][PF_6]$_2$ (9). To a CH_2Cl_2 solution (1 mL) of [Ni(NO)(bipy)][PF_6] (76 mg, 0.195 mmol) was added to a CH_2Cl_2 solution (1 mL) of 2,2-biypridine (14 mg, 0.092 mmol). When it was allowed to stand at room temperature for 2 h, a blue microcrystalline solid precipitated from the solution. The supernatant was decanted, and the precipitate was washed with hexanes and then dried in vacuo (21 mg, 43% yield). Anal. Calcd for $C_{30}H_{24}F_{12}N_{10}Ni_3O_4P_2$: C, 34.17; H, 2.29; N, 13.28. Found: C, 34.53; H, 2.08; N, 12.98. ^{1}H NMR (CD_3NO_2, 400 MHz, 22 °C): δ 7.29 (d, 2H, aryl H (bipy)Ni(O_2N_2), J_{HH} = 4 Hz), 7.41 (t, 2H, aryl H (bipy)Ni(O_2N_2), J_{HH} = 8 Hz), 7.99 (d, 2H, aryl H (bipy)Ni(O_2N_2), J_{HH} = 8 Hz), 8.02 (s, 4H, aryl H (bipy)Ni(NO)$^+$), 8.10 (t, 2H, aryl H (bipy)Ni(O_2N_2), J_{HH} = 8 Hz), 8.32 (m, 8H, overlapping aryl H (bipy)Ni(NO)$^+$), 10.35 (s, 4H, aryl H (bipy)Ni(NO)$^+$). ^{31}P{^{1}H} NMR (CD_3NO_2, 163 MHz, 22 °C): δ −144.7 (sept, PF_6^-, J_{P-F} = 711 Hz). ^{19}F{^{1}H} NMR (CD_3NO_2, 376 MHz, 22 °C): δ −73.27 (d, PF_6^-, J_{P-F} = 707 Hz). IR (CH_3NO_2, cm^{-1}): 1828 (s, ν_{NO}). IR (Nujol mull, cm^{-1}): 1836 (s, ν_{NO}).

X-ray Crystallography. Data for **3**, **6**, and **9** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (α = 0.71073 Å). The crystals were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. Data were collected using ω scans with 0.5° frame widths. Frame exposures of 10, 20, and 20 s were used for **3**, **6** and **9**, respectively. Data collection and cell parameter

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determination were conducted using the SMART program.[75] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[76] Absorption correction of the data was carried out using the multiscan method SADABS.[77] Subsequent calculations were carried out using SHELXTL.[78] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[78] A summary of the relevant crystallographic data for complexes **3**, **6**, and **9** can be found in Table 1.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, crystallographic details (as CIF files), and spectral data for compounds **3**–**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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