DOI: 10.1002/ejic.200800256

# Reactivity of the Radical NO with a Masked Form of 14 Valence Electron (PNP)Rh: Forming Rh(0, I or II)?

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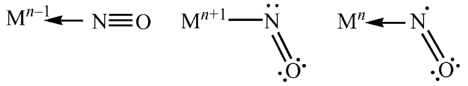
**Keywords:** Homogeneous catalysis / Nitrogen oxides / Pincer ligand / Radical reactions / Redox chemistry

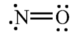
The reaction of NO with $[(t\mathrm{Bu}_2\mathrm{PCH}_2\mathrm{SiMe}_2)\mathrm{NSiMe}_2\mathrm{CH}_2\mathrm{P}t\mathrm{Bu}(\mathrm{CMe}_2\mathrm{CH}_2)]\mathrm{RhH}$, a functional equivalent of "(PNP)Rh," rapidly forms (PNP)Rh($N_2$) and (PNP)Rh(NO)($NO_2$). Detected intermediates include (PNP)Rh(NO), characterized by its NMR, EPR and IR spectra as well as by DFT calculation, as having the neutral NO-centered radical Lewis base donating to $Rh^{I}$. One other intermediate is detected, using a combination of spectroscopic and DFT methods, as containing a nitrite (O–N=O) ligand that is *O*-bound to Rh, giving an overall $C_s$ symmetry. The overall reaction is thus the disproportionation of NO catalyzed by $Rh^{I}$, and the reaction serves to produce nonradical products from radical NO.

## Introduction

The coordination chemistry of NO has been recognized as chameleon-like for over 40 years,[1–5] beginning with the first determination of a nonlinear bonding geometry (i.e., nonlinear MNO angle), originally identified as $NO^{-1}$, in contrast to the linear bonding mode of $NO^+$. In terms of hybridization, "linear NO" has sp nitrogen while bent NO has $sp^2$ nitrogen. The latter is analogous to RNO (R = alkyl or aryl) in terms of hybridization and bonding.

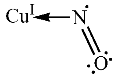


More recently, a third bonding type, the neutral, ligand-centered radical NO, has been identified.[6–8] It is generally formed when: a) the $L_nM$ moiety to which reagent NO bonds does not support the 1-electron redox change implied by conversion to the $NO^+$ or $NO^-$ bonding modes and b) the $L_nM$ fragment possesses a 16-valence electron count, and so "seeks" a traditional (2-electron donor) Lewis base. Under those circumstances, $L_nM$ prefers the nitrogen lone pair in Lewis structure **A**, and bends NO in that fashion. This is true of $Ru^{2+}$ and $Co^{3+}$.



**A**

This is decidedly *not* true of $Co^{2+}$ (prefers $Co^{3+}$ and $NO^-$, hence forming bent CoNO) or $Fe^{3+}$ (prefers $Fe^{2+}$ and $NO^+$, hence linear FeNO). However, in a porphyrin environment, $Fe^{2+}$ reacting with NO presents some of the most structurally and electronically complex chemistry known, precisely because of the ambivalence of the choice of "best" redox states, and this has been reviewed at length.[9,10] The puzzling chemistry[6] of $Cu^{I}$ (not reducible!) with diatomic NO is best understood by NO functioning as a traditional Lewis base, hence NO is apparently also unable to oxidize $Cu^{I}$ to $Cu^{II}$, which would yield a $Cu^{II}$ bent nitrosyl ($NO^-$); the observed result is redox state **B**.



**B**

This MNO geometry, where intermediate (ca. 145°) bending is dictated not by a lone pair on N, but by only a single electron in a $sp^2$ orbital on nitrogen, is conveniently termed a "half-bent" nitrosyl. As a result of the spin density of this primary product, it is reactive towards additional NO, leading to N/O bond cleavage, N/N bond formation, and net disproportionation of NO. Late-transition-metal complexes of neutral NO are rare[6,7] and thus warrant further study, particularly to define their reactivity.

We report here on a seemingly simple case leading to the ligand-centered radical $NO^0$ bound to a metal, successful in part because the metal prefers 2-electron redox change ($Rh^{I}$), which is incompatible with the ±1e change typical of NO. The reagent metal complex has an even electron count, and is coordinatively unsaturated, so can easily form a Lewis acid/base adduct without need of redox change at nitrogen, yet any such 1:1 adduct, must have an odd electron (hence non-singlet ground state) count; the 18-electron rule cannot be obeyed. This leads to more complicated sub-

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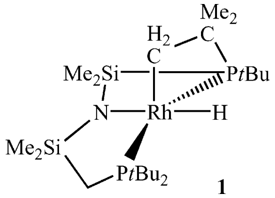
sequent reactions of the primary product. Ligand-centered radical character can be proven by spectroscopy, structure, and spin-density determination, supplemented with DFT calculations.

## Results

### General Reactivity

"(PNP)Rh" is[11] in fact [($t$Bu$_2$PCH$_2$SiMe$_2$)NSiMe$_2$CH$_2$P$t$Bu(CMe$_2$CH$_2$)]RhH (**1**), and thus Rh$^{III}$, but it functions as a masked source of Rh$^{I}$ because C–Rh–H reductive elimination (effectively yielding [($t$Bu$_2$PCH$_2$SiMe$_2$)$_2$N]Rh) is triggered by many attacking reagents.



**1**

The reaction of **1** with NO occurs in time of mixing at 25 °C, and can be best understood by studies at various mol ratios. The species detected are found to be very dependent on the Rh/NO mol ratio, characteristic of a multistep reaction where the primary product is as reactive towards NO as is **1** itself. At a 1:3 Rh/NO ratio, the product is (PNP)Rh(NO)(NO$_2$), which shows $C_s$ symmetry, with two $t$Bu and two SiMe proton NMR chemical shifts. This compound was also identified by single-crystal X-ray diffraction, which shows (Figure 1) a square-pyramidal structure with $N$-bound NO$_2$ basal and *trans* to the PNP amide N, and with bent NO apical (hence Rh$^{III}$). The IR spectrum of this molecule shows N/O stretching vibrations at 1677 and 1649 cm$^{-1}$. The nitro group has an Rh/N distance intermediate between the other two Rh/N bond lengths; the Rh–N(nitrosyl) bond is shortest. The nitrosyl group binds in a strongly bent form (121.1°), indicative of NO$^{-1}$. There is significant rotation of the nitrosyl out of the idealized mirror plane, and this may be responsible for Rh–P distances, which differ by 0.04 Å. Angles around the nitro N deviate from 120° by no more than 4.2°, and angles from the apical N3 to basal atoms range from 91.6 to 97.5°. The nitrosyl NO distance, 1.164(3) Å (bond order 2) is shorter than that in the NO$_2$ group, 1.203(8) and 1.236(8) Å (bond order 1.5). Altogether this supports the assignment of Rh$^{III}$ oxidation state with NO$^-$ and NO$_2$$^-$ ligands as the final product of the reaction of **1** with NO.

At Rh/NO mol ratios of 1:1 to 1:2, we detect varying amounts of two species formed before (PNP)Rh(NO)(NO$_2$), one of which is (PNP)Rh(N$_2$).[11] The other intermediate, (PNP)Rh(NO), can be detected at higher Rh/NO ratios. A second species, **I**, can be detected at intermediate ratios, yet is not observed at an Rh/NO ratio of 1:3.

### Characterization of (PNP)Rh(NO)

At a Rh/NO ratio of ca. 1:1, much of the Rh is found as a broad-lined set of $^1$H NMR signals in the ratio 12:36:4, and proposed to be due to an odd-electron 1:1 product, (PNP)Rh(NO); the chemical shifts of these three resonances (thus $C_{2v}$ symmetry) are in the range +10 to +2.2 ppm, and thus not shifted as much as those of some other paramagnetic (PNP)MX complexes.[12] The SiMe$_2$ $^1$H NMR resonance in particular, because it is the sharpest, proves $C_{2v}$ symmetry most persuasively. The infrared spectrum of this molecule shows a strong absorption at 1594 cm$^{-1}$ in pentane. The NMR spectrum of this solution was unchanged after an additional 12 h at 25 °C, and indeed (PNP)Rh(NO) survives at least 3 d in benzene solution at 23 °C under inert atmosphere. A DFT calculation of the geometry of (PNP)Rh(NO) showed only one minimum (Figure 2), starting either from linear/planar metal or bent/"flattened tetrahedral" metal structures. It is a four coordinate, planar species with a "half-bent" RhNO unit, signifying neutral NO binding to the metal by a nitrogen lone pair (**C**). This is predicted to leave the radical character on N (and O, because the spin is really in a $\pi^*_{NO}$ orbital), and thus the RhNO angle is not as small as for a truly sp$^2$-hybridized N (ca. 125°); it optimizes to 147.7°.

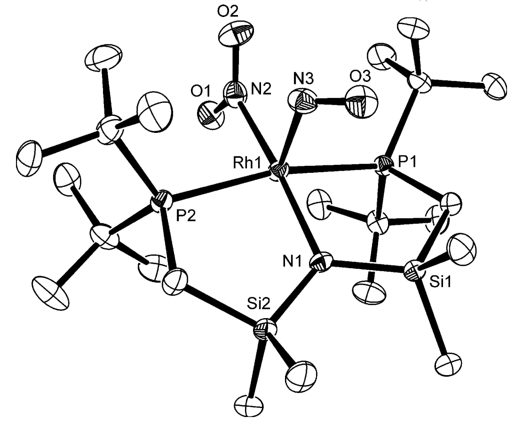


Figure 1. ORTEP drawing (50% probabilities) of the non-hydrogen atoms of (PNP)Rh(NO)(NO$_2$), showing selected atom labeling. Unlabeled atoms are carbon atoms. Selected structural parameters: Rh1–N3, 1.927(2)A, Rh1–N2, 2.093(7), Rh1–N1, 2.108(2), Rh1–P1, 2.3969(7), Rh1–P2, 2.4381(7), N3–Rh1–N2, 91.6(2)°; N3–Rh1–N1, 95.61(10), N2–Rh1–N1, 172.8(2), N1–Rh1–P1, 86.88(6), N3–Rh1–P1, 97.53(7), O2–N2–Rh1, 122.6(5), O1–N2–Rh1, 115.8(5), O2–N2–O1, 121.6(6), O3–N3–Rh1, 121.1(2), P1–Rh1–P2, 167.91(2).

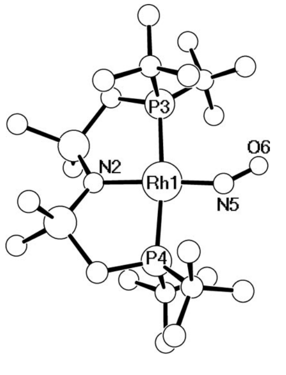
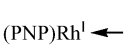
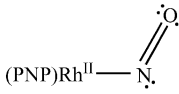


Figure 2. DFT-optimized geometry of (PNP)Rh(NO).



**C**



**D**

**E**

This assignment is confirmed by calculated spin densities of 0.61 on N and 0.35 on O. The localization of spins serves to explain the relatively small spread of $^1$H NMR chemical shifts, as well as the relatively sharp lines. The NO bond length of 1.198 Å is consistent with a double bond, compared to the calculated distance in free $N_2O$, identical at 1.198 Å. The calculated NO vibrational frequency is 1643 cm$^{-1}$. The DFT reaction energy for forming this 1:1 adduct is –41.0 kcal/mol.

The alternative charge distributions (redox states) are **D** ("fully" bent NO$^{-1}$, hence d$^7$ Rh$^{II}$) and **E** (linear NO$^+$, hence d$^9$ Rh$^0$), and their higher DFT energy indicates that arriving NO is neither an oxidizing (giving **D**) nor a reducing (giving **E**) reagent towards **1**. **E** might be especially unfavorable because d$^9$ Rh$^0$ would have a SOMO, which is $x^2$–$y^2$, hence strongly sigma antibonding. In sum, this potential 19/17-electron nitrosyl complex adopts a geometry, which gives it 18/16-valence electrons at M with an NO-centered radical ligand (**C**).

We have also observed (PNP)Rh(NO) by EPR spectroscopy. The X-band EPR spectrum of a toluene solution of 0.035 M (PNP)Rh(NO) was recorded at both 298 and 77 K. (Figures 3–4) The 298 K spectrum contains (Figure 3) a triplet that can be fit with a $g_{iso}$ value of 2.0064 and a hyperfine coupling constant $A_{iso}(^{14}N)$ = 36 MHz (13 G). The $g_{iso}$ value and the large $A_{iso}(^{14}N)$ and the lack of resolvable coupling to Rh and to PNP are consistent with an NO-centered radical.[7,8,13] Support for this interpretation comes from the contrasting EPR spectra at 298 K of the authentic Rh$^{II}$ (4d$^7$, $S$ = 1/2; 100% $^{103}$Rh, $I$ = 1/2) complexes, (PNP)RhX, where X = Cl or Br; these are both broad [7 times that of (PNP)Rh(NO) at 298 K], unstructured single peaks ($g \approx 2.3$), consistent with faster relaxation [vs. (PNP)Rh(NO)] due to metal-centered low-lying excited states. Also present in Figure 3 is a broad, featureless signal at $g$ = 2.10 that remains unassigned.

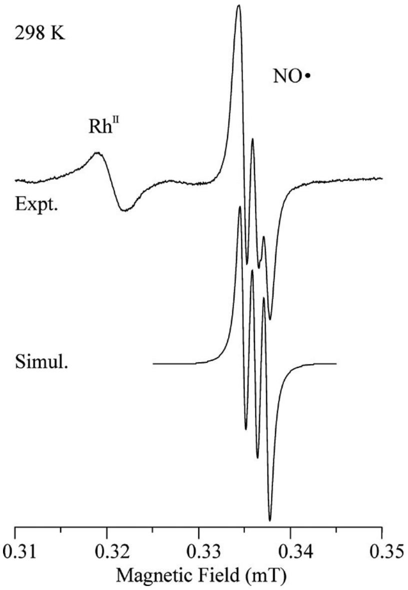


Figure 3. EPR spectrum (9.4389 GHz) recorded at 298 K of (PNP)-Rh(NO) in $CH_2Cl_2$ solution. Simulation (lower trace) parameters: $g_{iso}$ = 2.0064, $A_{iso}(^{14}N)$ = 36 MHz; Lorentzian linewidth, 18 MHz.

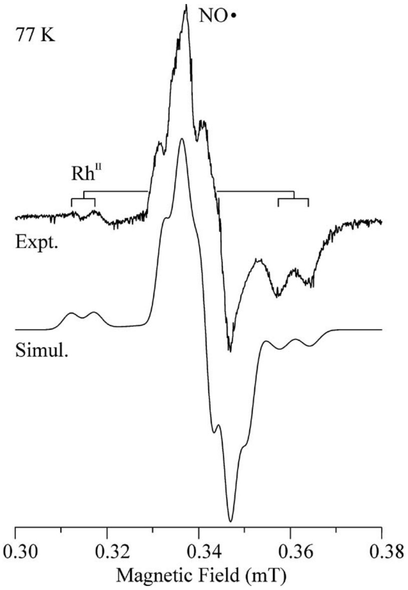


Figure 4. EPR spectrum (9.4238 GHz) recorded at 77 K of (PNP)-Rh(NO) in $CH_2Cl_2$ solution. Simulation (lower trace) is the sum of two separate sets of parameters, summed to approximate the experimental spectrum; set 1, NO-centered spin: **g** = [2.00500, 1.97, 1.94], $A_{iso}(^{14}N)$ = 100 MHz; Gaussian linewidth, 45 MHz; set 2, Rh-centered spin: **g** = [2.14, 1.97, 1.865], **A**($^{103}$Rh) = [150, 155, 170] MHz; Gaussian linewidth, 60 MHz. The parameters for the Rh-centered species are very approximate at $g_{mid}$.

The spectrum at 77 K (Figure 4) is dominated by a multiline spectrum that can be simulated as arising primarily from a slightly anisotropic species (**g** = [2.005, 1.970, 1.940]) with essentially isotropic hyperfine coupling to a single $^{14}$N [$A(^{14}N)$ = 100 MHz]. This average $g$ value {$g_{avg} = [(g_{max}^2 + g_{mid}^2 + g_{min}^2)/3]^{1/2}$ = 1.972} is much closer to 2.00 than is the case for the few authentic Rh$^{II}$ phosphanyl complexes (e.g., $g_{avg}$ = 2.17 for [Rh(TMPP)$_2$](BF$_4$)$_2$, where TMPP = tris(2,4,6-trimethoxyphenyl)phosphane,[14] $g_{avg}$ = 2.30 for [Rh(TMPP)(CN$t$Bu)$_2$](BF$_4$)$_2$ ,[15] and $g_{avg}$ = 2.137, 2.149 respectively, for two Rh$^{II}$ "piano-stool" complexes: [η$^1$:η$^6$:η$^1$-1,4-bis(diphenylphosphanyl)butyl]-2,3,5,6-tetramethylbenzene)rhodium(II) and [η$^1$:η$^6$:η$^1$-1,4-bis(diphenylphosphanyl)propoxy]-2,3,5,6-tetramethylbenzenerhodium(II).[16,17] The $g$ anisotropy {defined here as: $[(g_{max} - g_{min})/g_{avg}]$ = 0.033} is also much smaller than for the four listed Rh$^{II}$ complexes (respectively: 0.21,[14] 0.11,[15] 0.168,[17] 0.183[16]), all of which is more consistent with an NO-localized radical formulation of (PNP)Rh(NO) than as a Rh$^{II}$ complex.

An additional, weaker signal is observed at 77 K with doublet features (split by ca. 60 G) at both lower and higher magnetic fields than the dominant signal. This signal can be assigned to a Rh$^{II}$ species with **g** = [2.140, ca. 1.97, 1.865] ($g_{mid}$ presumably masked by the dominant signal), and with $\mathbf{A}(^{103}Rh)$ = [150, –, 170] MHz ($A_{gmid}$ cannot be determined). This $^{103}$Rh hyperfine coupling is in good agreement with that reported for authentic Rh$^{II}$ complexes [$A_{gmin}$ ≈ 170–180 MHz (ca. 62–66 G)].[15] This Rh$^{II}$ signal is presumably related to the broad, low field signal seen at 298 K.

## Formation and Reactivity of (PNP)Rh($N_2$)

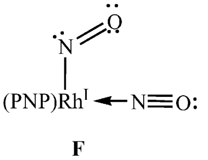
The concurrent formation and detection of an $N_2$ complex in this reaction under argon or vacuum is remarkable; such persistence requires a NO/Rh ratio of less than 2:1. Formation of $N_2$ arises because this is, fundamentally, a disproportionation of NO and $N_2$ is the reduced N. To better understand the formation of $N_2$, the reaction was repeated with altered stoichiometries: with excess Rh(0.8:1 NO/Rh ratio) and with a significant excess of NO(2.5:1 NO/Rh). The former experiment still showed nearly complete consumption of (PNP)Rh, and yet considerable production of (PNP)Rh($N_2$), as well as small amount of (PNP)Rh(NO)($NO_2$), but the major product(by $^1$H NMR) was (PNP)Rh(NO). The latter study (2.5:1 NO/Rh ratio) yielded (PNP)Rh(NO)($NO_2$) along with only a small amount of (PNP)Rh($N_2$). This suggests that (PNP)Rh($N_2$) is consumed by NO, a result which was confirmed by direct observation of this reaction using pure (PNP)Rh($N_2$).

## Mechanism

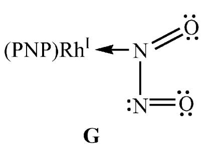
**a. N/N Bond-Formation Steps:** Clearly a reaction with 9 reagent molecules [Equation (1)] must proceed by a large number of elementary steps. Because the first-formed adduct (PNP)Rh(NO) is a radical and lacks an 18-electron configuration, the next step must produce a composition "(PNP)Rh$N_2O_2$," for which two connectivities are possible, **F** (attack of second NO on Rh) and **G** (attack on bound NO).

$$3\ (PNP)Rh + 6\ NO \rightarrow (PNP)Rh(N_2) + 2\ (PNP)Rh(NO)(NO_2) \quad (1)$$

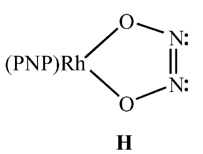
A key goal, given the ultimate need to form $N_2$, is the N/N bond formation. This has begun only in **G**. Moreover, **G** is a natural product of coupling the radical NO with the nitrosyl N, the highest spin density atom on (PNP)Rh(NO).



**F**



**G**



**H**

Experimentally, at a ratio of ca. 1.3:1 for NO/Rh, a new species **I** is detected; the $^1$H and $^{31}$P NMR of this species indicate $C_s$ symmetry, consistent with (PNP)Rh(X)(Y), where the ligands X and Y (which could be connected) decrease the symmetry below $C_{2v}$. The other requirement is that the observed species **I** be diamagnetic, which means it cannot have the odd-electron formula "(PNP)Rh$N_3O_3$."

A DFT geometry optimization shows **F** and **G** to be stationary states, but their free energy is not significantly below that of separated (PNP)Rh(NO) and NO (see Supporting Information), and thus excluded as identities for the observed species **I**. It is of interest that the dinitrosyl species (Figure 5)[18] has both RhNO units bent (122.9 and 124.1°; unlike drawing **F**) and hence contains Rh$^{III}$ with two NO$^-$; this indicates that Rh is a 2-electron reducing agent towards the pair of nitric oxide molecules. The geometry optimization of the species **G** rearranges to a structure where *both* N are binding to Rh (Figure 5). Given the bad energetics of both these structures, we studied structures where the ONNO ligand binds to Rh in a bidentate fashion through two O atoms. This optimized to a $C_{2v}$ symmetric structure **H** where both $Si_2N$–Rh–O angles are 142°. It lies 12.8 kcal/mol below the separated particles (PNP)Rh(NO) + NO, and has two N/O single bonds and an N/N double bond. It is thus the conjugate base of HON=NOH, and thus the two NO have oxidized Rh$^I$ by two electrons. This species obviously represents progress on the path to $N_2$ formation, but cannot be the observed species **I**, because its symmetry is too high vs. experiment. Several other structures were located (see Supporting Information) but their energies are not consistent with the experimental observations. Finally, we evaluated the structures of both the observed product and its nitrito isomer, (PNP)Rh(NO)(ONO), which is square pyramidal with apical NO and $C_s$ symmetry. The nitrito species lies 8.2 kcal/mol above the nitro isomer, and so is suggested as the identity of the observed intermediate **I**. Because this species disappears only slowly unless free NO is present, we propose that free NO can catalyze an otherwise slow nitrite-to-nitro linkage isomerization reaction of **I** to form (PNP)Rh(NO)($NO_2$).

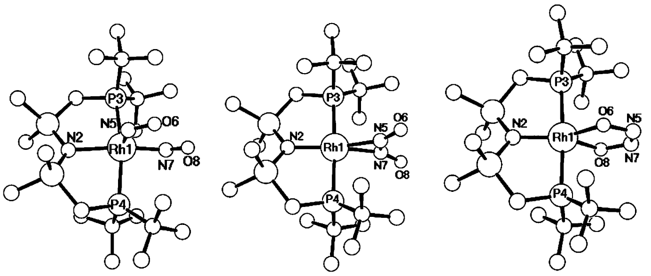
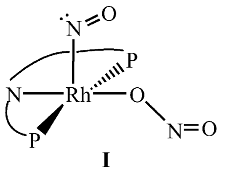


Figure 5. DFT-optimized geometries of (PNP)Rh$(NO)_2$, (PNP)Rh($N_2O_2$) and (PNP)Rh(ONNO).



**I**

This identity of observed intermediate **I** thus fails to give insight into the mechanism at the point where NO reacts with "(PNP)Rh$N_2O_2$," except to show that N/O bond formation (i.e. making ONO ligand) happens during the reaction, and that the nitrite linkage isomer is a kinetic product. The lack of accumulation of this next intermediate "(PNP)Rh$N_3O_3$" to detectable concentration probably relates to its being a radical, hence more reactive than its predecessor.

**b. Possible O-Atom Transfer Mechanisms:** With regard to that earlier mechanistic step, an unobserved species "(PNP)Rh$N_2O_2$" could next collide with (PNP)Rh(NO) to form (PNP)Rh($N_2O$) and (PNP)Rh($NO_2$); (PNP)Rh($N_2O$) will decay to the observed product (PNP)Rh($N_2$) by oxygen transfer, either to another (PNP)Rh(NO) or to "(PNP)Rh$N_2O_2$" or directly to NO itself. (PNP)Rh($NO_2$) would bind another NO to form the observed product (PNP)Rh(NO)($NO_2$). We do not favor the production of free $N_2O$ because we feel that it would not be competitive (vs. NO) for rebinding to any Rh.

The above mechanism involves reactions between two (PNP)Rh complexes for O-atom transfer. However, we have in the past[12] generally argued that the steric bulk of (PNP)$MX_n$ complexes is so large that such reactions are ineffective; this is why, for example, such complexes do not dimerize, by halide bridging, but instead exist as monomers. Thus, an alternative mechanism would involve free NO accepting an O atom from "(PNP)Rh$N_2O_2$" to produce free $NO_2$, which then combines efficiently with (PNP)Rh(NO) to give the final product.

## Discussion

The electron configuration $\{MNO\}^9$ has been little studied,[1,19,20] (in contrast[9] to $\{MNO\}^7$) and those few examples, of NO on $Pt^{II}$, are poorly studied, certainly without EPR characterization. The results for (PNP)Rh(NO), both computational and experimental, are consistent with a heavy component of spin density on the NO ligand, so this diatomic radical behaves more like a conventional Lewis base than like a radical, until its subsequent reactivity is considered. That subsequent reactivity involves quenching radical character. As stated above, this net reaction is:

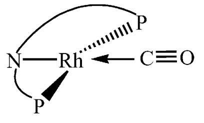
$$2\ Rh^{I} + 6\ NO \rightarrow N_2 + 2\ NO^{-}_{2} + 2\ NO^{-} + 2\ Rh^{III}$$

where the $NO_2$ and NO in the product complexes have also undergone Rh-mediated electron transfer to give coordinated $NO^-$ and $NO_2^-$. However, deleting identical species on both sides of the reaction yields, more simply:

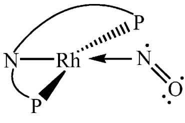
$$4\ NO \rightarrow N_2 + 2\ NO_2$$

It is thus truly nitrogen disproportionation, catalyzed by Rh redox equivalents and by binding to Rh. The reason that the reaction does not stop at simple coordination of one ligand to the metal is that this 1:1 adduct, while it has 16/18 electrons at Rh, has radical character at the nitrosyl N, so it retains latent reactivity, which is "quenched" by radical coupling to additional NO. The species (PNP)Rh($N_2O_2$), effects oxygen transfer to ultimately lead to coordinated $N_2$. The chemistry of NO thus is complicated because multiple equivalents of NO per metal are required to satisfy the 18-electron rule (and to form even-electron nitrogen species); these principles control enthalpic preferences.

The series of molecules **2**–**4**[21,22] show dramatic change in structure and bonding associated with sequential addition of one nuclear proton and one electron to atom E in the Rh/E/O substructure.



**2**



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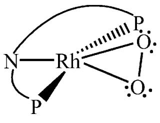

**4**

Among these, the $\pi^*_{EO}$ orbitals of the free diatomic EO, respectively, contains zero, one, and two electrons. As one moves along this series, it is energetically productive first to rehybridize atom E (**2**→**3**), then to get the O atom involved in the bonding to Rh (**3**→**4**). In this process, EO moves towards twofold symmetry, and thus the $\pi^*$ orbital becomes less polarized on atom E. This yields full redox chemistry (not merely back donation) in **4**, where the $\pi^*_{OO}$ has dropped enough in energy that it gains a significant share in the electrons of what began as $Rh^I$. However, for **3**, it is not yet redox chemistry, since NO functions there as a Lewis base towards Rh, and the rehybridization is merely to put the odd electron on the NO, by a $(\pi^*_{NO})^1$ configuration.

## Experimental Section

**General:** All reactions were performed in a glove box or on a Schlenk line using standard air-sensitive techniques, involving only argon or vacuum. Solvent distillation was carried out using either Na/benzophenone, $CaH_2$, 4-Å molecular sieves, a Grubbs-type purification system, or a combination of these four methods. Solvents were degassed and stored in airtight glassware. [($t$$Bu_2PCH_2SiMe_2$)$NSiMe_2CH_2P$$t$Bu($CMe_2CH_2$)]RhH (**1**) was prepared following the published synthesis.[11] $^1$H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents. $^{31}P\{^1H\}$ spectra are referenced to external standards of 85% $H_3PO_4$ (at 0 ppm). NMR spectra were recorded with a Varian Gemini 2000 (300 MHz $^1$H; 121.5 MHz $^{31}$P), or a Varian Inova instrument (400 MHz $^1$H; 162 MHz $^{31}$P; 100.6 MHz $^{13}$C). Gas reactions were carried out with a calibrated gas line with the solution being first degassed and 2.2 mL of headspace assumed for the NMR tube. Infrared spectra were recorded with a Nicolet 510P FT-IR spectrometer. ESI mass-spectra were recorded with a PE-Sciex API III Triple Quadrupole mass spectrometer in THF solutions. EPR spectra were obtained with a Bruker 300EMX spectrometer operating at X-band (ca. 9.5 GHz); microwave power, 10 mW (298 K), 0.1 mW (77°K); modulation amplitude, 1.0 G, modulation frequency, 100 kHz. EPR spectra were simulated using the program QPOWA, written by Belford and co-workers, as well as WinEPR.

### Reaction of 1 with NO

**a. Rh/NO ca. 1:1:** [($t$$Bu_2PCH_2SiMe_2$)$NSiMe_2CH_2P$$t$Bu($CMe_2CH_2$)]RhH (**1**) (0.0236 g, 0.0428 mmol) was dissolved in $C_6D_6$ (0.6 mL) in a J-Young NMR tube. This solution was freeze-pump-thawed three times and one equivalent of NO was added by gas line. The tube was shaken and NMR recorded. $^{31}$P NMR (161.98 MHz, $C_6D_6$), $\delta$ = 61.30 [d, $^1J_{PRh}$ = 131.0 Hz, (PNP)Rh($N_2$), 49%], 58.60 [d, $^1J_{PRh}$ = 129.2 Hz, (PNP)Rh($NO_2$)(NO), 32%], 51.41 (d, $^1J_{PRh}$ = 143.7 Hz, I, 19%) ppm. $^1$H NMR (400.12 MHz, $C_6D_6$) (PNP)Rh(NO): $\delta$ = 10.10 (s, width at half height $J$ = 31.4 Hz, 4 H, Si-$CH_2$-P), 4.23 (s, width at half height $J$ = 78.6 Hz, 36 H, $t$Bu), 2.24 (s, width at half height $J$ = 10.6 Hz, 12 H, Si-$CH_3$) ppm. (PNP)Rh($N_2$): 1.300 (virtual triplet, $^3J_{HP}$ 12.5 Hz, , 36 H, $t$-Bu), 0.71 (virtual triplet, $^2J_{HP}$ = 9.7 Hz, 4 H, Si-$CH_2$-P), 0.33 (s, 12 H, Si–

$CH_3$). (PNP)Rh($NO_2$)(NO): 1.316 [virtual triplet, overlapped with *t*Bu signal of (PNP)Rh($N_2$), 18 H], 0.94 (virtual triplet, $^3J_{HP}$ = 13.5 Hz, 18 H, *t*Bu), 0.36 (s, 6 H, Si-$CH_3$), 0.33 (s, 6 H, Si-$CH_3$). **I**: 1.17 (virtual triplet, $^3J_{HP}$ = 12.9 Hz, 18 H, *t*Bu), 0.79 (virtual triplet, $^3J_{HP}$ = 12.5 Hz, 18 H, *t*Bu), 0.52 (s, 6 H, Si-$CH_3$), 0.40 (s, 6 H, Si-$CH_3$) ppm. According to $^1$H NMR the ratio (PNP)Rh($NO_2$)(NO)/(PNP)Rh(NO) is 1:3. The solvent was removed in vacuo and the residue was dissolved in pentane. IR (pentane solution): $\tilde{\nu}$ = 1594 (PNP)Rh(NO), 2092 (PNP)Rh($N_2$) $cm^{-1}$.

**b. Rh/NO ca. 1:2:** Compound **1** (0.0105 g, 0.019 mmol) was dissolved in $C_6D_6$ (0.6 mL) in a J-Young NMR tube. This solution was freeze-pump-thawed three times and 2 equiv. of NO was added by gas line. $^{31}$P NMR shows the following percentage of products: (PNP)Rh($N_2$) 35%, (PNP)Rh($NO_2$)(NO) 55%, **I** 11%. $^1$H NMR shows the ratio (PNP)Rh($NO_2$)(NO)/(PNP)Rh(NO) = 2:1, hence much less (PNP)Rh(NO) than in **a** above.

**c. Rh/NO ca. 1:2.5:** Compound **1** (0.0192 g, 0.033 mmol) was dissolved in $C_6D_6$ (0.5 mL) in a J-Young NMR tube. This solution was freeze-pump-thawed three times and 2.5 equiv. of NO were added by gas line. The tube was shaken and formation of some brownish precipitate on walls of the tube was observed. $^{31}$P NMR (121.47 MHz, $C_6D_6$): $\delta$ = 61.13 [d, $^1J_{PRh}$ = 130.0 Hz, (PNP)Rh($N_2$), 12%], 58.42 [d, $^1J_{PRh}$ = 128.3 Hz, (PNP)Rh($NO_2$)(NO), 68%], 53.7 [d, $^1J_{PRh}$ = 119.9 Hz, (PNP)Rh(NO)Cl, 20%] ppm. $^1$H NMR (300.06 MHz, $C_6D_6$), for (PNP)Rh($NO_2$)(NO): $\delta$ = 1.31 (virtual triplet, $^3J_{HP}$ = 13.5 Hz, 18 H), 0.94 (virtual triplet, $^3J_{HP}$ = 13.5 Hz, 18 H, *t*Bu), 0.90 (virtual triplet, $^2J_{HP}$ = 11.6 Hz, 2 H, Si-$CH_2$-P), 0.84 (virtual triplet, $^2J_{HP}$ = 11.0 Hz, 2 H, Si-$CH_2$-P), 0.36 (s, 6 H, Si-$CH_3$), 0.33 (s, 6 H, Si-$CH_3$) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $C_6D_6$) for (PNP)Rh($NO_2$)(NO): $\delta$ = 36.66 (m, *C*-$CH_3$), 30.54 (virtual triplet, $^2J_{PC}$ 5.3 Hz, C-$\mathit{CH}_3$), 28.38 (virtual triplet, $^2J_{PC}$ = 4.6 Hz, C-$\mathit{CH}_3$), 12.11 (m, Si-C-P), 6.55 (virtual triplet, $^3J_{PC}$ = 4.6 Hz, Si-$\mathit{CH}_3$), 6.05 (virtual triplet, $^3J_{PC}$ = 3.8 Hz, Si-$\mathit{CH}_3$) ppm. After 12 h (by $^{31}$P NMR), the relative concentration of (PNP)Rh($N_2$) decreased approximately 2.5 times. The solvent was removed in vacuo, the residue dissolved in $Et_2O$ (precipitate on walls did not dissolve) and crystals for X-ray analysis were obtained by slow evaporation of the $Et_2O$ solution. IR and mass spectra were obtained following crystallization. ESI-MS: *m*/*z* (%) = 581.5 (100) [(PNP)Rh(NO)]$^+$ (calcd. 581.2). IR (pentane solution): $\tilde{\nu}$ = 1677, 1649 $cm^{-1}$. The presence of (PNP)RhCl(NO) was established by recording the $^{31}$P NMR spectrum of the crystallographic sample, which contained some amount of this chloride analog, together with (PNP)Rh(NO)($NO_2$); the chloride was an impurity [(PNP)RhCl] in the synthesis of **1**.

**d. Rh/NO 1:3:** This reaction, conducted under conditions similar to those for 2.5 NO, shows no (PNP)Rh($N_2$) in the reaction mixture immediately after addition of NO (according to $^{31}$P NMR). Only (PNP)Rh(NO)($NO_2$) was seen.

**Reaction of (PNP)Rh($N_2$) with NO:** (PNP)Rh($N_2$) (0.0103 g, 0.0178 mmol) was dissolved in $C_6D_6$ (0.6 mL) in a J-Young NMR tube. This solution was freeze-pump-thawed three times and three equivalents of NO were added by gas line. The $^{31}$P NMR shows (PNP)Rh($N_2$), 68% and (PNP)Rh($NO_2$)(NO), 32%. After 4 h from addition, a precipitate formed on the walls of NMR tube (see above) and $^{31}$P NMR shows complete conversion to (PNP)Rh($NO_2$)(NO).

CCDC-677130 [for (PNP)Rh(NO)($NO_2$)] contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ui/data_request/cif.

**Supporting Information** (see also the footnote on the first page of this article): Crystallographic and DFT computational details.

## Acknowledgments

This work was supported by the National Science Foundation (NSF) (NSF-CHE-0544829).

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[18] For (PNP)Rh$(NO)_2$, starting geometries involved a square pyramid with bent/bent, bent/linear, linear/bent and linear/linear structures. These converged to the structure in Figure 5, or rotamers of these due to rotation about the Ru-bent NO bond.

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Received: March 11, 2008