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Radical (NO) and Nonradical (N_2O) Reagents Convert a Ruthenium(IV) Nitride to the Same Nitrosyl Complex

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The ruthenium(IV) nitride complex (PNP)RuN (PNP = (^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N$^-$) reacts rapidly with 2NO to form (PNP)Ru(NO) and N_2O, via no detectable intermediate. The linear nitrosyl complex has a planar structure. In a slower reaction, (PNP)RuN reacts with N_2O by O-atom transfer (established by ^{15}N labeling) to give the same nitrosyl complex and N_2. Density functional theory (B3LYP) calculations show both reactions to be very thermodynamically favorable. Analysis of possible intermediates in each reaction shows that radical (PNP)RuN(NO) has much spin density on nitride N (hence, N^{2-}), while one 2 + 3 metallacycle, (PNP)RuN$_3$O, has the wrong connectivity to form a product. Instead, an intermediate with a doubly bent N_2O (hence, a two-electron reduced *N*-nitrosoimide form) brings the O atom in proximity to the nitride N on the path to a product.

The recent synthesis[1] of (PNP)Ru^{IV}N opens the question of the reactivity of this RuN unit: nucleophilic or electrophilic? Learning to control the reactivity of such a terminal nitride will be an essential step in the conversion of N_2 to amines and heterocycles, for example. We report here high-yield reaction chemistry which shows the ability of this molecule to react with two different nitrogen oxides, one a radical (NO) and the other an even-electron species (N_2O). Both nitrogen oxides yield the same (and diamagnetic) metal-containing product but by reactions involving very different processes. The discovery of two paths for production of the same ruthenium product enables some interesting thermodynamic conclusions to be drawn. In contrast to N_2O reactions exhibited by oxophilic early transition metals,[2,3] the results reported here show no transfer of oxygen to the metal.[4,5] Finally, there is no experimental determination of the structure[6] of a coordinated N_2O, and the present work makes some contribution to that subject as well as to the surface chemistry of metal nitrides with nitrogen oxides.

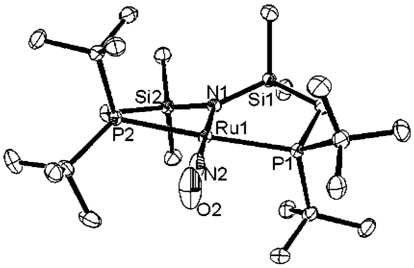

Figure 1. ORTEP drawing (50% probability) of the non-H atoms of (PNP)Ru(NO) showing labels of the non-C atoms. Selected structural parameters: Ru–N1, 2.0695(16) Å; Ru–N2, 1.7213(19) Å; Ru–P1, 2.3834(5) Å; N2–O2, 1.185(3) Å; N1–Ru–N2, 179.21(9)°; P1–Ru–P2, 173.043(19)°; Ru–N2–O2, 179.2(2)°.

Reaction[7] of (PNP)Ru^{IV}N with NO (~1:1 mole ratio to avoid degradation of the product by a local excess of NO) in benzene at 22 °C is complete in time of mixing to give a new product whose ^{1}H and ^{31}P NMR spectra indicate C_{2v} symmetry and display an NO stretch in the IR at 1691 cm^{-1} (an Et$_2$O solution). An electrospray ionization mass spectrum gives a peak consistent with formula (PNP)Ru(NO), and an X-ray diffraction structure determination of crystals grown from Et$_2$O (Figure 1) shows the molecule to be a Ru^0 complex with a linear RuNO unit. The other product in this balanced reaction (eq 1) is nitrous oxide (detected by IR in

$$\text{(PNP)RuN} + 2\text{NO} \rightarrow \text{(PNP)RuNO} + \text{N}_2\text{O} \qquad (1)$$

toluene or in Et$_2$O at 2217 cm^{-1}), so the first NO effects a three-electron reduction (eq 2). When the reagents are

$$\text{N}^{3-} + \text{NO} \rightarrow \text{N}_2\text{O} + 3\text{e}^- \qquad (2)$$

combined below −78 °C in toluene, no intermediate is detected by ^{31}P or ^{1}H NMR. One sees only unreacted (PNP)RuN and product (PNP)Ru(NO), with conversion to the latter increasing as the temperature is slowly raised. No paramag-

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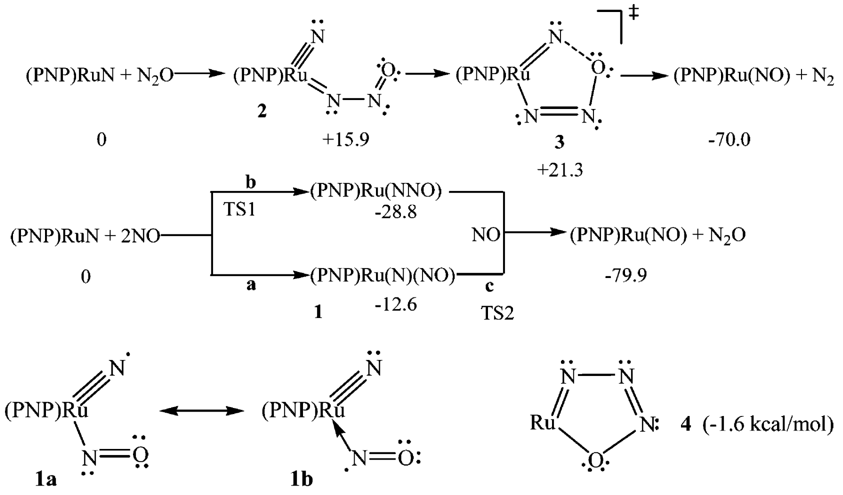
Scheme 1. Reaction Electronic Energies (kcal/mol)



netically shifted ^{1}H NMR signals due to a 1:1 intermediate “(PNP)RuNNO”, or any subsequent species “(PNP)RuN$_3$O$_2$” reach detectable concentration. Thus, the rate-determining step occurs at the first encounter of (PNP)RuN with NO. Reaction of (PNP)Ru^{15}N with isotopically normal NO shows (^{15}N and ^{31}P NMR and IR evidence) (^{15}N)NO and isotopically normal (PNP)Ru(NO). The reaction is thus N atom transfer from Ru to NO, not O atom transfer to nitride.[8]

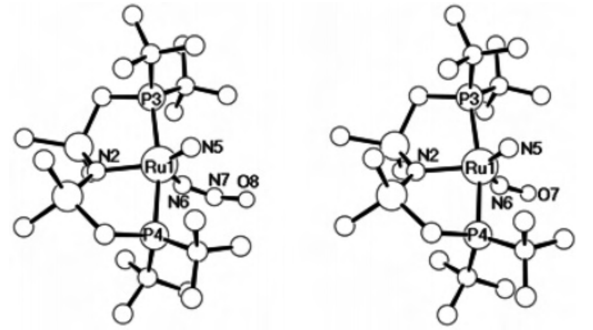
Remarkably, the reaction[7] of (PNP)RuN with N$_2$O (excess; $\sim$2 atm) in benzene at 22 °C also produces (PNP)Ru(NO) in a reaction which shows a different (i.e., nonradical) aspect of the reactivity of this nitride complex. The reaction is much slower than that with NO, requiring 2 days to go to completion to form this single metal complex. The balanced reaction (eq 3) could be accomplished by either O atom transfer to RuN (i.e., N$_2$−O bond cleavage) or N atom transfer to RuN (i.e., N−NO bond cleavage). When the

$$(\mathrm{PNP})\mathrm{RuN} + \mathrm{N_2O} \rightarrow (\mathrm{PNP})\mathrm{RuNO} + \mathrm{N_2} \tag{3}$$

reaction is carried out with labeled (PNP)Ru(^{15}N) and isotopically normal N$_2$O, ^{15}N NMR shows the ruthenium product to be (PNP)Ru(^{15}NO) (344 ppm, t, $J_{\mathrm{NP}} = 6.5$ Hz). The reaction is thus O atom transfer.[9]

Density functional theory (DFT; B3LYP) calculations[7] provide energetic and structural information on several potential intermediates in the mechanisms of both reactions. As shown in Scheme 1, the overall reactions with both NO and N$_2$O are highly favorable energetically. Consistent with the rapid rate observed experimentally, the reaction with NO begins (a or b in Scheme 1) with very energetically favorable 1:1 adduct formation. Does the first NO attack Ru (a) or nitride (b)? The deeper minimum is b, which is also sterically better, where the first NO reduces Ru by three electrons (eq 2). Thus, although the reagent Ru is four-coordinate and it is exergonic to bind NO at Ru, attack at the nitride ligand gives the more thermodynamically favorable intermediate and forms the good leaving group N$_2$O. This intermediate has C_{2v} symmetry (η^1-linear N$_2$O), and thus [(PNP)Ru]^0 is unable to reduce N$_2$O; 97% of the spin density in this radical is on Ru, so this is Ru$^{\mathrm{I}}$ coordinating neutral N$_2$O. We have sought minima where η^1-N$_2$O is singly bent at either the terminal or the central N, or doubly bent at both N atoms, and find that these all optimize to the C_{2v} structure. The second NO oxidizes this Ru$^{\mathrm{I}}$, becoming bent NO$^-$ ($\angle$RuNO $= 124.4°$) in this radical-quenching step.[7]

The radical complex **1** from the less exothermic step a (Figure 2) has remarkable spin densities **1a** (0.00 at N6, 0.02 at O7, and only 0.06 at Ru and 0.01 at PNP amide N); the spin density (0.84) is mainly on the nitride N, where it is thus prepared to couple to the second arriving NO radical; the alternative Lewis structure **1b** contributes negligibly. This spin density at nitride N, creating N^{2-} radical character, shows that coordination of NO to Ru effects redox chemistry not so much at the metal but that an electron-rich nitride ligand is especially vulnerable to oxidation by electron-poor NO$^\bullet$. The bent NO in (PNP)RuN(NO) becomes linear in step c (Scheme 1),[7] promoting the loss of N$_2$O. Adding a ligand to an unsaturated metal is expected to have no major barrier, so we located transition states (TS1 and TS2) for forming N−N bonds. TS2 (Scheme 1) has the lower free energy (by



2 **1**

Figure 2. DFT (B3LYP)-optimized structures. Right, **1**, (PNP)RuN(NO): Ru−N2, 2.17 Å; Ru−N5, 1.74 Å. Left, **2**, (PNP)RuN(N$_2$O): Ru−N2, 2.14 Å; Ru−N5, 1.64 Å; Ru−N6, 2.16 Å; N6−N7, 1.20 Å; N7−O8, 1.26 Å; Ru−N6−N7, 126.7°; N6−N7−O8, 133.6°.

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2.8 kcal/mol), with a long N−N distance (1.85 Å) and a strongly bent ∠N···NO (112.1°), as these radical centers couple in the faster paths a and c.

The N_2O reaction can begin with adduct formation (Figure 2). Species **2** is bent[7] to near sp^2 hybridization at both N6 and N7, consistent with Lewis structure **2** (an *N*-nitrosoimide of Ru^{VI}), which leads naturally to the metallacycle **3** (Ru^{IV}), where N−O bond formation has begun; **3** is found to be the transition state associated with O atom transfer. The energy of binding N_2 to (PNP)Ru(NO) in species (PNP)Ru(NO)(N_2),[7] 11.1 kcal/mol, is calculated to be comparable to the unfavorable $T\Delta S$ for adduct formation, so N_2 release is spontaneous. The energy of **2** is too high to reach an observable concentration. We also sought alternative structures. Remarkably, the species **4** from 1,3-addition of N═N═O across the Ru≡N bond with an orientation opposite from that of **3** is slightly more stable (electronic energy) than the separated particles, so the $\Delta G°$ for its formation[10] will be 0 ± 5 kcal/mol. Because both five-membered rings have satisfactory Lewis structures, it is remarkable that **3** and **4** differ in energy by 22.9 kcal/mol. Clearly, **4** lacks the connectivity needed to form RuNO, and therefore, **4** is a dead end, not an intermediate on the reaction path.

Returning to the question which begins this contribution, these results show a versatility of (PNP)RuN to participate in both radical and nonradical reactions. The nonradical reaction (N_2O) relies on the nucleophilic character of the nitride (N^{3-}), in (PNP)RuN(N_2O), together with a new "doubly bent" binding mode (**2**) of N_2O to a metal vulnerable to oxidation to give the *N*-nitrosoimide form (hence, a large reorganization of the N_2O electronic structure), which simultaneously brings its O atom close to the nitride N. The O atom transfer has a reasonable mechanism due to a very plausible metallacycle transition state. One mechanism of the radical reaction (NO) involves the initially bound NO creating radical character on the nitride in (PNP)RuN(NO), **1a**, by partial oxidation of that center, followed by radical−radical annihilation [i.e., (Ru)N−N(O) coupling] to form a transient containing the good leaving group, N_2O. The surprisingly favorable thermodynamics for both reactions can be attributed to the stability of electron-rich $(PNP)Ru^-$ bound to π-acidic NO^+, as well as the favorable coproducts N_2 and N_2O. Given the large swing of the Ru oxidation state in the reaction, this is not merely the reactivity of N^{3-} but of the entire reagent RuN^+ unit.

Because ν_{NO} of (PNP)Ru(NO) is among the lowest recorded for a neutral molecule containing a linear MNO unit [surpassed only by TpW(NO)(PMe_3)(η^2-olefin)[11] Cp*W(NO)R_2,[12] and WX_3(NO)(pyridine),[13] with X = OR or NR_2, all near 1550 cm^{-1}], the (PNP)Ru fragment has strong reducing power. This enables recognition here of the two-electron-reduced *N*-nitrosoimide bonding to a metal (**2**), whose conformational flexibility facilitates O atom transfer.

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Supporting Information Available: Full computational and experimental details and spectroscopic data (including DFT calculations), together with applicable CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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