Communication

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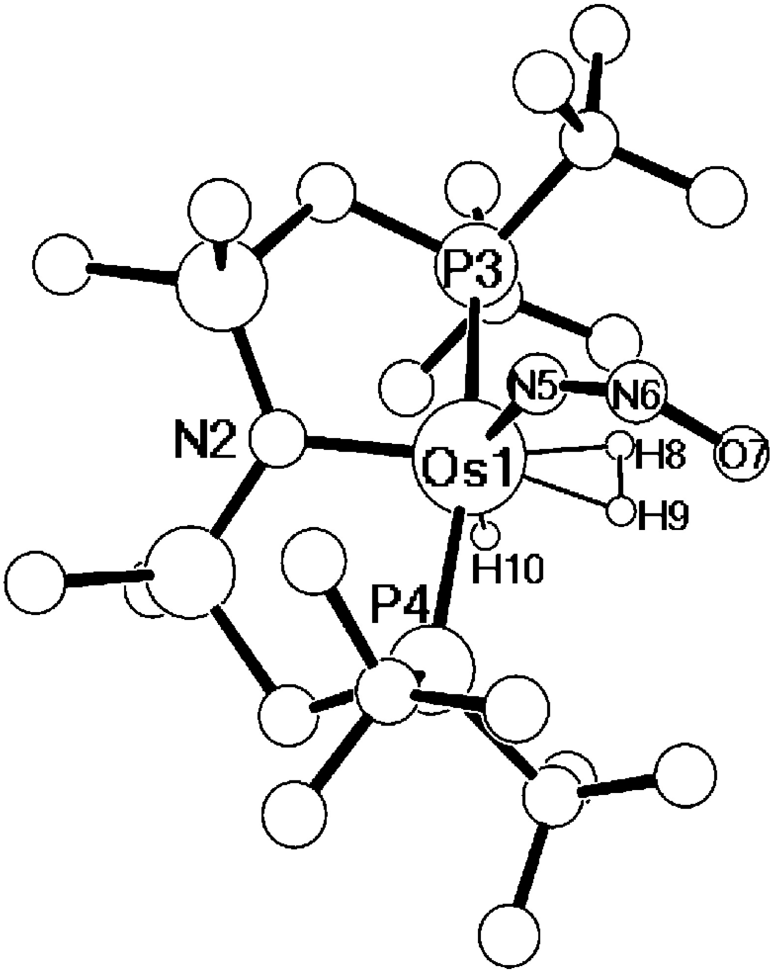

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Facile Hydrogenation of N_2O by an Operationally Unsaturated Osmium Polyhydride

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Nitrous oxide is a molecule whose promise as an oxygen atom transfer reagent is richer than the reality.[1−4] The anticipated oxidizing power of an O-atom transfer (oxidizing a metal or another nitrogen oxide), together with the liberation of stable N_2, rarely has been realized in practice, probably for a combination of kinetic reasons which may originate from the weak donor power of N_2O as a ligand. A rare example of cleavage of the N/N bond of N_2O left any Mo-coordinated N_2O intermediate undetected.[5] Indeed, there is no crystal structure determination of coordinated N_2O.[6,7] N_2O is reduced to N_2 and oxide by certain divalent Ti, V, Cr, and Ru complexes.[8−10] We describe here the result of a study of the reaction of N_2O with an operationally unsaturated[11] metal complex carrying enough hydride ligands that one might have some optimism for observing hydrogenation of N_2O.[12,13] In fact, the work shows additional insights beyond even these anticipated ones, including the conversion of N_2O to water.

Reaction of $(PNP)Os(H)_3$[14] where PNP = $N(SiMe_2CH_2P^tBu_2)_2$ with 1 atm N_2O in benzene at 22 °C occurs within 1 h to give complete conversion to a single product whose proton and ^{31}P NMR spectra indicate C_s molecular symmetry.[15] The implication is a product (PNP)OsX(Y); a hydride signal at −34.8 ppm indicates that X = H, and the selectively hydride-coupled ^{31}P NMR spectrum is a doublet, confirming the presence of only one hydride. The hydride chemical shift is sufficiently far upfield that it indicates an empty site trans to itself.[16] There is no evidence of any released H_2 (neither free H_2 ^1H NMR at ~4.5 ppm, nor by reactive trapping[14] of free H_2 with added $(PNP)Os(H)_2$(C-aryl)). A ^1H NMR signal is seen at 0.5 ppm in the product solution and is significantly broad. The source of the 0.5 ppm signal can be vacuum transferred out of the sample, giving a signal in the resulting osmium-free C_6D_6 solution that duplicates the signal of authentic water dissolved in C_6D_6. The ^1H NMR of the nonvolatile fraction after vacuum transfer showed the absence of this signal. In addition, the 0.5 ppm signal in the unseparated reaction product mixture grows at that chemical shift upon addition of water. The infrared spectrum of the product complex showed no absorption in the region 2000−1480 cm^{-1}, where any multiple N/O bond would be expected. An absorption observed at 2004 cm^{-1} is attributed to a N_2 ligand in $(PNP)OsH(N_2)$; this is a low frequency compared to relevant Os(II)/N_2 complexes,[17] indicating strong donor power of the amide chelate ligand to the OsN_2 unit. Reaction of $(PNP)Os(H)_3$ with 99% $(^{15}N)_2O$ gives an isotopically labeled analogue product whose ^{15}N NMR spectrum shows two chemical shifts, at values consistent with other osmium N_2 complexes,[18] each signal showing mutual coupling of 4.6 Hz; the ^{15}N NMR peak at −107.9 ppm, assigned[18] to the N directly bonded to Os, also shows (doublet of) triplet character due to J_{PN} = 2 Hz. The infrared spectrum of this sample shows the N/N stretch isotopically shifted to 1948 cm^{-1}.

In search for any intermediate, $(PNP)Os(H)_3$ in toluene-d_8 was combined with N_2O (1 atm, 10 equiv) at low temperature, and ^1H and ^{31}P NMR spectra were recorded (following 5 min for equilibration at each temperature) at 10 °C intervals beginning at −60 °C. Only $(PNP)Os(H)_3$ was detected until about −10 °C, where the product described above becomes visible. Water (too broad to detect confidently at −10 °C) is readily detected beginning about 20 °C. No intermediate thus reaches detectable concentration under these conditions, and the slow step in the reaction is thus the endergonic first step, binding of N_2O to $(PNP)Os(H)_3$. Low equilibrium binding of such a poor ligand is consistent with literature precedent on N_2O as a very poor ligand.

$(PNP)OsH(N_2)$ reacts[15] within 10 min at 22 °C with 0.33 atm (3 equiv) added CO in benzene, to give complete conversion to an adduct, $(PNP)OsH(N_2)(CO)$, of C_s symmetry (^1H and ^{31}P NMR) and revealing IR stretching frequencies at 2104 and 1988 and 1896 cm^{-1}. The hydride chemical shift, −3.8 ppm, indicates the presence of a ligand trans to hydride and thus suggests coordination number six. Longer reaction times, or addition of more CO, does not cause further reaction at 22 °C, including no production of $(PNP)OsH(CO)_2$; N_2 binding is robust. More "oxidizing" ligands are more aggressive in releasing N_2. $(PNP)OsH(N_2)$ reacts[15] with 1 atm H_2 over 24 h to give $(PNP)Os(H)_3$. $(PNP)OsH(N_2)$ reacts with acetylene (4 equiv) in benzene to give a 1:1 adduct containing η^2-HCCH.

Strong acids react in an unusual fashion.[15] Since protonation of $(PNP)OsH(N_2)$ could occur at Os, at the hydride, or at N_2, it is surprising that the selectivity is none of these, but rather protonation at the chelate amide nitrogen, to give $(PN(H)P)OsH(N_2)^+$ as its BF_4 or triflate salts; the N/N stretching frequency for this molecule is higher by 48 cm^{-1} than that for $PNPOsH(N_2)$, consistent with the assigned protonation site. Both of these salts are soluble in benzene, but the identity of their NMR spectroscopic parameters suggests that the anions are not coordinated, and that the species present is the Os(II) cation. The NH proton has a chemical shift of ~3 ppm and integrates correctly versus other protons in the ion; the observed anion (BF_4^- vs TfO^-) dependence of this chemical shift is consistent with variable hydrogen bonding of the NH proton to the different anions. The hydride chemical shift, −38.2 ppm, again indicates a square pyramidal structure with no ligand trans to hydride. All of these conclusions are confirmed by a single-crystal X-ray structure determination (Figure 1). Over 24 h, the triflate salt of this cation transforms[15] to a species with a hydride chemical shift inconsistent with coordination number five, with the absence of an NH proton, and with intensity 2 hydride signal. All of this is consistent with the formula $(PNP)Os(H)_2OTf$. This shows that it is the conversion from Os(II) to Os(IV) that triggers the loss of N_2, consistent with higher oxidation states having poor ability to bind N_2. In general then, $(PNP)OsH(N_2)$ is a poor Lewis acid (it does not detectably bind additional N_2 and shows no $(PNP)OsH(N_2)(H_2)$ as an intermediate in its (slow) reaction with H_2), and the N_2 serves as a leaving group in the reactions reported here.

DFT (B3LYP) calculations (Scheme 1) on potential intermediates in this N/O hydrogenation reaction are revealing.[15] Adduct **1** demonstrates the operationally unsaturated character of (PNP)Os-

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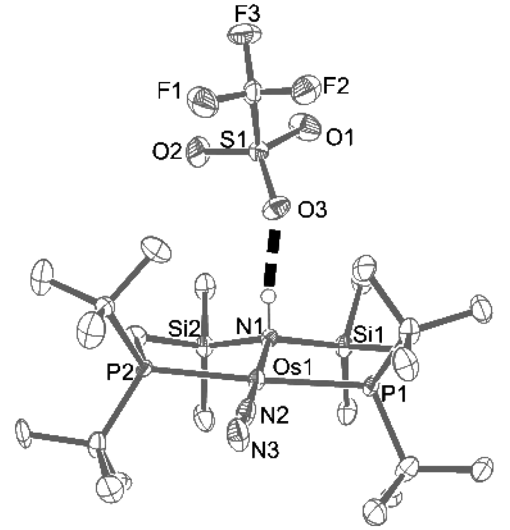
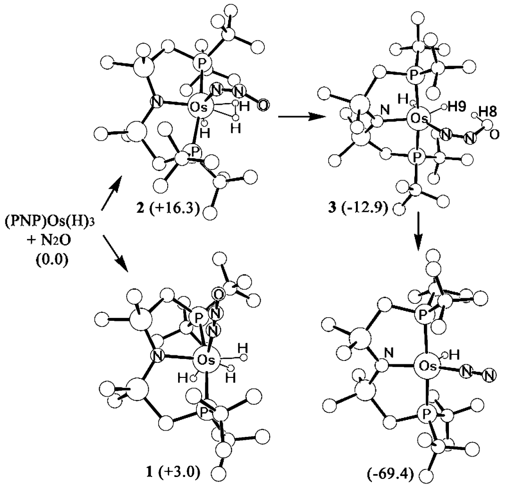


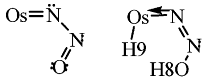
Figure 1. ORTEP drawing (50% probability ellipsoids) of the non-hydrogen atoms of $[PN(H)P]OsH(N_2)^+$ ion paired with triflate. Unlabeled atoms are carbon. The hydride hydrogen was not located. The N1···O3 distance is 2.923 Å.

Scheme 1 ^{a}



^{a} Electronic energies in kcal/mol.

$(H)_3$, in that the multiple (amide N)/Os bond there lengthens by 0.12 Å as this N-bound N_2O adduct forms. However the Os(IV) d^4 character makes the N_2O bind only poorly. This energy is consistent with the lack of observation of any adduct at low temperature. Higher in energy than **1** (by 13.3 kcal/mol) is a doubly bent binding mode **2**, which suggests a redox transformation to N_2O^{2-} (**2**), which brings the oxygen in a more suitable position (vs **1**) to receive H intramolecularly. The claim of redox behavior is supported by the finding that this species (**2**) contains a H_2 ligand (0.92 Å between these H), which means two hydrides are oxidized as N_2O is reduced. Given the high Brønsted acidity of coordinated H_2, this feature of **2** is ideal for forming the next suggested intermediate **3**. This species is $(PNP^{-1})Os(H^{-1})_2(-N{=}N-OH^{-1})$, thus Os(IV), and **3** shows an attractive interaction (1.69 Å) between the hydroxyl H8 and the hydride H9, **3**. The overall reaction, releasing water, is found to be highly exothermic.



2 **3**

Phenyl azide, isolobal with N_2O, reacts[15] with $(PNP)Os(H)_3$ to form $(PNP)OsH(N_2)$ and aniline.[19] The reaction is complete in ~12 h in benzene. There is no NMR evidence for coordination (nor hydrogen bonding) of aniline to $(PNP)OsH(N_2)$.

In summary, the ability of $(PNP)Os(H)_3$ to hydrogenate the N/O bond of N_2O derives from the ability of this operationally unsaturated $(H)_2Os^{IV}$ complex to transfer two electrons to N_2O, thus creating doubly bent N_2O^{2-}, as well as the potential for high valent Os to prefer H_2 rather then 2 H^-, and the resulting high Brønsted acidity normally associated with coordinated H_2; kinetically facile migration of protons then effects the formation of H_2O. This is rather different from the action of a Cu^I_4 assembly in nitrous oxide reductase.[20] A recent DFT study of this enzyme recognized the fact that bending N_2O lowers the energy of the LUMO but failed to describe their observations in terms of an *N*-nitrosoimide and did not use the term two-electron reduction, but rather "back-bonding". Since CO stretching frequencies show Cu^I to be a very poor π-donor,[21] it is interesting that proteins overcome this deficiency by binding two coppers to a single N_2O, and still N_2O is bound very weakly (by less than 5 kcal/mol). Single and multiple metals thus find complementary ways to promote electron transfer to and structural rearrangement of N_2O.

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Supporting Information Available: Full synthetic spectroscopic and computational details along with crystallographic details (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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