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Nitric Oxide Abstracts a Nitrogen Atom from an Osmium Nitrido Complex To Give Nitrous Oxide

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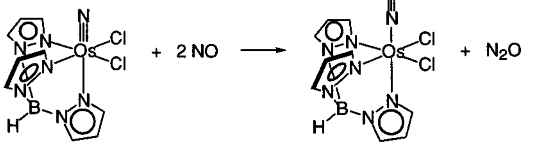
The chemistry of nitric oxide, NO, is attracting widespread interest, from environmental to biological chemistry.[1,2] As a free radical, NO reacts rapidly with other odd-electron species, such as superoxide and alkyl radicals, and reversibly dimerizes to N_2O_2. NO can be oxidized to NO^+ or to NO_2^- (by formal addition of $O^{\bullet-}$). Reduction of NO to N_2O commonly occurs via deoxygenation of N_2O_2, often in a metal-mediated process.[3] Reported here is the first example of reduction of NO to N_2O that occurs by one-step nitrogen-atom transfer.

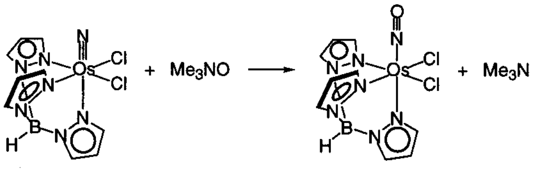
Stirring a benzene solution of the osmium nitrido complex $TpOs(N)Cl_2$ (**1**)[4] under ∼0.75 atm of NO for 24 h results in stoichiometric conversion to N_2O and the osmium nitrosyl complex $TpOs(NO)Cl_2$ (**2**)[5] (eq 1; Tp = $HBpz_3$, hydrotris(pyrazolyl)borate).[6] The osmium stoichiometry was determined by ^1H NMR and the N_2O was detected by gas-phase IR. The IR spectrum of N_2O at moderate pressures (∼0.10 Torr), using a low-resolution PE1600 FT-IR, shows broad R and P branches, with maxima at 2214 and 2238 cm^{-1} and a minimum at 2224 cm^{-1} (the unobserved Q-branch position; Figure 1). The yield of N_2O was 90 ± 10%, based on a Beer's law calibration at 2224 cm^{-1} and subtraction of the residual N_2O present in the NO reactant (Figure 1, inset).[7] Kinetic data obtained by ^1H NMR in CD_2Cl_2 under 3 atm of NO (pseudo-first-order conditions) are consistent with first-order decay of **1**. Reducing the pressure by a factor of 3 increases the half-life by roughly the same factor. Reaction **1** thus appears to be first order in both **1** and NO, with rate constant $k \approx 3 \times 10^{-4}$ M^{-1} s^{-1} at 21 °C.[8]



(1)

1 **2**

There are two reasonable types of mechanisms for reaction 1. The nitrosyl complex **2** could be formed by oxygen atom transfer to the nitrido ligand in **1**, analogous to the conversion of **1** to **2** by Me_3NO (eq 2).[9] In reaction 1, the source of oxygen could be from an NO-derived species such as bound or free N_2O_2. Alternatively, addition of NO to the nitrido ligand would form the osmium−N_2O complex, $[TpOs(NNO)Cl_2]$ (Scheme 1). Loss of N_2O would give $[TpOsCl_2]$, which would be converted to **2** by the excess NO present. An ^{15}N-labeling experiment can distinguish the two pathways because the first incorporates the nitrido ligand into the nitrosyl group, while the second converts the nitrido ligand into the terminal nitrogen of the N_2O. The reaction of $TpOs(^{15}N)Cl_2$[4] with ^{14}NO supports the second pathway (Scheme 1), as only $TpOs(^{14}NO)Cl_2$ is formed by IR and mass spectroscopies [<10% $Os(^{15}NO)$]. Gas-phase IR spectra of the volatiles from the reaction show both the residual $^{14}N^{14}NO$ impurity in the NO (unobserved Q branch at 2224 cm^{-1}) and a new feature at lower frequency whose R branch overlaps with the P branch of $^{14}N^{14}NO$ (Figure 1, bottom). The Q branch minimum of the new feature at 2201 cm^{-1} agrees at this level of resolution with the 2202.5 cm^{-1} reported for $^{15}N^{14}NO$.[10]



(2)

1 **2**

Direct, rate-limiting attack of NO on the nitrido ligand of **1** is consistent with the apparent bimolecular kinetics. Facile dissociation of N_2O from $[TpOs(NNO)Cl_2]$ is reasonable given the lability of the one known N_2O complex.[11,12] Attempts to observe an N_2O complex by running the reaction under N_2O (g) gave a more complex reaction mixture including precipitate(s) which have not yet been characterized. When the reaction of **1** plus NO is run in 80% CD_2Cl_2/20% CCl_4 instead of CD_2Cl_2, the major product is $TpOsCl_3$ (**3**),[4b] with only a 5% yield of **2**. The inclusion of some CCl_4 solvent appears to cause a small increase in the rate of disappearance of **1**. These results support the intermediacy of $[TpOsCl_2]$ which can be trapped either by NO or by CCl_4 (Scheme

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(2) See, for instance: (a) *Science* **1992**, *258*, 1861, 1862−3 (molecule of the year). Stamler, J. S.; Singel, D. J.; Loscalzo, J. *Science* **1992**, *258*, 1898−1902. (b) McKenney, D. J.; Drury, C. F. *Global Change Biol.* **1997**, *3*, 317−326. (c) Parvulescu, V. I.; Grange, P.; Delmon, B. *Catal. Today* **1998**, *46*, 233−316. (d) Burney, S.; Caulfield, J. L.; Niles, J. C.; Wishnok, J. S.; Tannenbaum, S. R. *Mutat. Res. Fund. Mol. Mech. Mutagen.* **1999**, *424*, 37−49.

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(4) (a) Crevier, T. J.; Mayer, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5595−5596. (b) Crevier, T. J.; Bennett, B. K.; Bowman, J. A.; Soper, J. D.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminski, W.; Mayer, J. M. *J. Am. Chem. Soc.* In press.

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(6) In a typical procedure, NO (0.658 atm in a 139 mL bulb, 3.74 mmol) was condensed at 77 K onto **1** (42.7 mg, 87.3 μmol) and dry degassed benzene (30 mL). The reaction was stirred for 12 h at ambient temperatures, changing color from orange to brown. The volatiles were transferred to an evacuated gas-phase IR cell. The reaction solution was evaporated to dryness, and its IR and ^1H NMR spectra matched those of independently prepared **2**.[5]

(7) (a) The IR extinction coefficient at 2224 cm^{-1} under our conditions was 8.3×10^{-4} $Torr^{-1}$ cm^{-1}. (b) Research-grade NO contains small amounts of N_2O, which we have not been able to quantitatively remove; for a very recent approach to N_2O removal from NO, see: Lorkovi, I. M.; Ford, P. C. *Inorg. Chem.* **2000**, *39*, 632−633, footnote 7.

(8) (a) The concentration of NO in CH_2Cl_2 is assumed to be the same as that in CCl_4 [Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids*; Wiley: New York, 1991; p 272], 1.42×10^{-2} M under 1 atm of pressure. (b) See also: Shaw, A. W.; Vosper, A. J. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1239−1244.

(9) Reference 5, following: Williams, D. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 823−4.

(10) Begun, G. M.; Fletcher, W. H. *J. Chem. Phys.* **1958**, *28*, 414−8; $\nu_{^{14}N^{15}NO} = 2177.6$ cm^{-1}.

(11) The only known simple complex of N_2O, $[Ru(N_2O)(NH_3)_5]^{2+}$, is quite labile: Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 6874−6. Diamantis, A. A.; Sparrow, G. J. *J. Chem. Soc., Chem. Commun.* **1970**, 819−820.

(12) Alternatively, bound N_2O could be displaced by NO or CCl_4.

10.1021/ja002833v CCC: $19.00

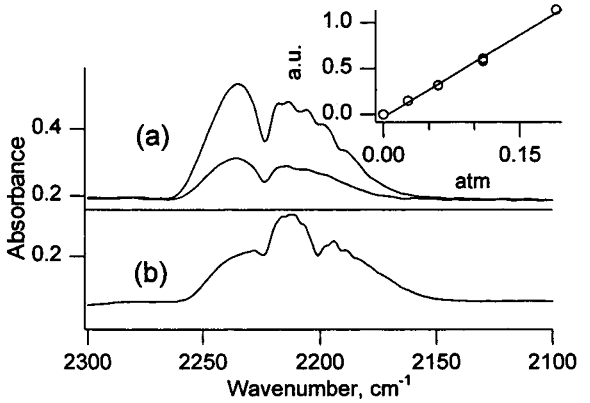
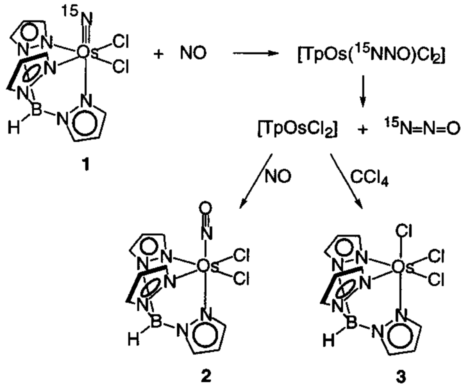


Figure 1. (a) Gas-phase IR spectra of the residual N_2O in the NO reactant (lower trace) and the larger amount of N_2O in the volatiles after reaction with $TpOs(N)Cl_2$ (upper trace). Inset: Beer's law plot at 2224 cm^{-1}. (b) Gas-phase IR spectrum of the volatiles from $TpOs(^{15}N)Cl_2$ plus ^{14}NO.

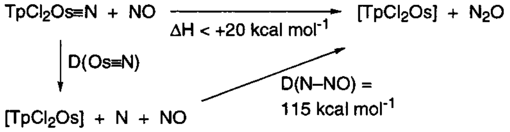
Scheme 1



1). $[TpOsCl_2OTf]^-$, which is an alternative source of $[TpOsCl_2]$, also reacts with NO and CCl_4 to give **2** and **3**, respectively.[13]

Nitrogen atom transfer from a metal nitrido to another metal is well precedented,[14] but to our knowledge this is the first example of N-atom transfer to a nonmetal substrate. The electrophilic and oxidizing character of **1** seems to be important to the NO addition reaction. $TpOs(N)(OAc)_2$, which reacts with BPh_3 in the same manner as **1**,[15] also appears to form a nitrosyl complex on treatment with NO. This is based on the reaction mixture showing an IR band at 1869 cm^{-1}. However, the less electrophilic $TpOs(N)Ph_2$[4] is unreactive with NO (as is Mn(N)(salen)[16]).[17] In the reverse direction, Cummins et al. have reported the remarkable removal of a nitrogen atom from N_2O by a molybdenum−tris(amido) complex, in a reaction that appears to require two molybdenum centers.[18] To our knowledge, the analogous addition of NO to a metal−oxygen multiple bond to give a nitrite complex is not known, although photolysis of metal nitrite complexes can give NO[19] and the addition of NO to coordinated dioxygen has been described.[20]

Scheme 2



The relatively facile transfer of N from **1** to NO provides an upper limit on the Os≡N bond strength. The reaction $\mathbf{1} + NO \rightleftarrows [TpOsCl_2] + N_2O$ has a barrier in the forward direction $\Delta G^\ddagger = 22$ kcal mol^{-1} so it is conservative to estimate $\Delta G° < +20$ kcal mol^{-1}. Since $\Delta S° \sim 0$ eu for this equilibrium, $\Delta G° \cong \Delta H°$. Adding N to NO to give N_2O is exothermic by 114.9 kcal mol^{-1}.[21] Coupling these values in a thermochemical cycle gives $D(Os\equiv N) < 135$ kcal mol^{-1} (Scheme 2).

The ability of **1** to add NO is consistent with the general reactivity of this class of osmium(VI) nitrido complexes: reactions typically involve both reduction of the osmium and bond formation to the nitrido ligand. For instance, Cp_2Co induces N−N coupling, forming $[TpCl_2Os^{III}(N_2)Os^{II}Cl_2Tp]^-$, and amines and carbanions add to the nitrido ligand to form reduced hydrazido and amido complexes.[4,22] In a number of ways the chemistry of **1** is the reverse of the reactivity of the Cummins molybdenum−tris(amido) system:[23] coupling vs cleavage of N_2, and formation vs consumption of N_2O by nitrogen atom transfer. The reactivity inversion reflects the underlying thermochemistry, that molybdenum(III) amides are strongly reducing and the Mo≡N bond is very strong (155.3 ± 3.3 kcal mol^{-1} [24]) while osmium(VI) nitrido complexes such as **1** are oxidants and have weaker Os≡N bonds (<135 kcal mol^{-1}).

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[17] The related 2,2′:6′,2″-terpyridine-nitrido complex $[(tpy)Os(N)Cl_2]PF_6$ reacts with 0.53 atm of NO in CH_3CN overnight but IR spectra of a complex mixture of products do not indicate the presence of the known nitrosyl complex $[(tpy)Os(NO)Cl_2]PF_6$: Williams, D. S.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 823−4.

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