The Nitrous Oxide Complex, $RuCl_2(\eta^1\text{-}N_2O)(P{-}N)(PPh_3)$ (P−N = [*o*-(*N,N*-Dimethylamino)phenyl]diphenylphosphine); Low Temperature Conversion of N_2O to N_2 and O_2

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Nitrous oxide (N_2O) is a potent greenhouse gas and regulator of atmospheric ozone concentrations.[1] The major anthropogenic sources of N_2O emissions include nitric and adipic acid syntheses, land cultivation, biomass burning, and combustion of fossil fuels,[2] while natural emissions of N_2O result from bacterial nitrification and denitrification processes.[3] Nitrous oxide reductase, a Cu-containing enzyme that catalyzes the terminal step of denitrification (i.e. the two-electron reduction of N_2O to N_2 and H_2O), is currently a subject of intense interest; an X-ray crystal structure[4] and solution studies[5] have demonstrated that the enzyme contains the first example of a Cu−S cluster in one of its active sites. N_2O also continues to attract interest as a potentially clean and highly selective oxygen-atom donor for catalytic oxidation processes.[6] For example, processes for the oxidation of benzene to phenol using N_2O over Fe or Ru/ZSM-5 zeolites have been demonstrated by Solutia (formerly Monsanto).[6j,k]

Although N_2O does react with several metal complexes, it is generally regarded as kinetically inert toward reduction and a "poor" ligand;[6i] however, findings presented below imply that such a description is not justified. The formation of metal−oxo species (with concomitant extrusion of N_2) is a common theme,[6i,7] while the insertion of N_2O into a metal−carbon bond unaccompanied by loss of N_2 is rare.[8] Other reactions involve the net insertion of an oxygen atom into metal−hydride[9] or metal−carbon[9a,10] bonds to yield hydroxy, alkoxy, or aryloxy metal complexes. An important development was the unprecedented demonstration of reductive denitrification of N_2O to yield metal nitride and nitrosyl complexes.[11] Despite the intense current interest in transition metal-mediated N_2O activation, no metal complexes containing the N_2O ligand have been identified since the original reports of $[Ru(NH_3)_5(N_2O)]^{2+}$ and possibly $[Ru(NH_3)_5]_2(\mu\text{-}N_2O)^{4+}$ by Armor and Taube about 30 years ago.[12] We describe here the in situ synthesis and NMR characterization of an η^1-N_2O complex, again of Ru(II); the N_2O binds at the vacant site of the highly reactive, five-coordinate species $RuCl_2(P{-}N)(PPh_3)$ (**1**) (P−N = [*o*-(*N,N*-dimethylamino)phenyl]diphenylphosphine) (Figure 1), which is also known to form complexes with so-called "weak" ligands such as H_2S[13] and thiols.[14]

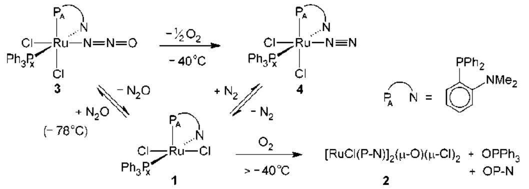

Figure 1. Summary of the chemistry described.

When a green solution of **1** in CD_2Cl_2 is placed under 1 atm of N_2O at 20 °C,[15] no immediate reaction is detected by $^{31}P\{^1H\}$ NMR spectroscopy. After 2 days, the diamagnetic dimetallic Ru(III) complex $[RuCl(P{-}N)]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ (**2**) is formed along with the phosphine oxides $OPPh_3$ and OP−N, and N_2.[16] An ORTEP diagram of this interesting μ-oxo complex is shown in Figure 2.[17] When a CD_2Cl_2 solution of **1** is treated with 1 atm of N_2O (or ^{15}NNO) at −78 °C, a greenish yellow solution results and NMR spectra reveal rapid formation of the adduct, *cis*-$RuCl_2(\eta^1\text{-}N_2O)(P{-}N)(PPh_3)$ (**3**). The species is stable below −40 °C, and is characterized by inequivalent *N*-methyl resonances in the ^1H

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(15) N_2O and ^{15}NNO were purchased from Matheson and used as received.

(16) ^1H NMR data for **2** (NMe_2 region, CD_2Cl_2, −78 °C): overlapping signals in the δ 2.0−3.5 region; $^{31}P\{^1H\}$ NMR δ 38.2 d, 39.4 d ($^4J_{PP}$ = 10.1 Hz). The phosphine oxides were characterized independently by the in situ reactions of P−N and PPh_3 with H_2O_2; the N_2 and O_2 were detected in the headspace above the reaction mixture by GC analysis.

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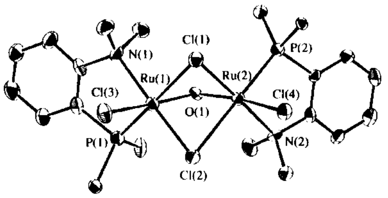

Figure 2. The ORTEP diagram for $[RuCl(P-N)]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ (**2**) with thermal ellipsoids drawn at 50% probability; H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2**: Ru(1)−Ru(2), 2.9173(7); Ru(1)−O(1), 1.921(4); Ru(2)−O(1), 1.926(4); Ru(1)−O(1)−Ru(2), 98.6(2); Ru(1)−Cl(1)−Ru(2), 71.92(4); Ru(1)−Cl(2)−Ru(2), 71.25(5).

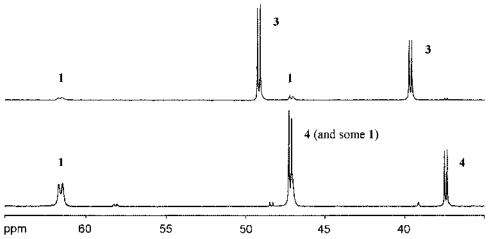

Figure 3. $^{31}P\{^1H\}$ NMR spectra (121.4 MHz, CD_2Cl_2, −78 °C) of $RuCl_2(\eta^1\text{-}N_2O)(P-N)(PPh_3)$ (**3**) and $RuCl_2(\eta^1\text{-}N_2)(P-N)(PPh_3)$ (**4**) generated from $RuCl_2(P-N)(PPh_3)$ (**1**) under 1 atm of N_2O or N_2, respectively.

NMR spectrum[18] (confirming a *cis*-dichloro geometry[13]), a well-resolved AX pattern in the $^{31}P\{^1H\}$ NMR spectrum (Figure 3), and most importantly a singlet at δ125.8 in the ^{15}N NMR spectrum, which is assigned to the η^1-coordinated ^{15}NNO ligand. The observed upfield δ_N shift of ~25 ppm relative to uncoordinated N_2O[18] is consistent with ligation via the terminal nitrogen. Solid-state ^{15}N NMR data for ^{15}N-labeled N_2O adsorbed on vanadia−titania surfaces[19] and in zeolites[20] support terminal N-coordination, and in particular Hu and Apple[19] have shown that the chemical shift of the central-N of N_2O remained nearly constant upon adsorption of the gas while an upfield shift of ~25 ppm in the terminal-N signal was observed. The balance of evidence for the coordination mode of the weakly bound N_2O in $[Ru(NH_3)_5(N_2O)]^{2+}$ (X-ray powder diffraction, IR, and electronic spectra data and mechanistic insight from formation of the complex from $[Ru(NH_3)_5NO]^{3+}$) also strongly favors bonding through the terminal-N.[21]

When the low-temperature-stabilized CD_2Cl_2 solution of **3** is warmed to −40 °C, gradual decomposition to the known η^1-N_2 complex *cis*-$RuCl_2(\eta^1\text{-}N_2)(P-N)(PPh_3)$ (**4**) occurs, as indicated by the presence of a characteristic AX pattern in the $^{31}P\{^1H\}$ NMR spectrum;[13a,22] **4** is also formed by treating **1** with N_2 (Figure 3). At −40 °C, O_2 is produced from **3** concomitantly with **4**, and no decomposition to the μ-oxo species (**2**) or phosphine oxide is seen.[16] The nature of the conversion of the N_2O to N_2 and O_2 (which is catalytic) remains uncertain; a bimolecular process (cf. ref 11) seems more likely than a unimolecular one. Above −40 °C, the μ-oxo species (**2**) and phosphine oxides begin to form (Figure 1). Of note, the uncatalyzed conversion of N_2O to N_2 and O_2 requires elevated temperatures (>600 °C), while heterogeneously catalyzed conversions on metal oxides and zeolites have been observed at ~100 °C.[23] At below −40 °C, the stoichiometries of the conversions between **1**, **3**, and **4** are as shown in Figure 1, but at higher temperatures when the phosphine oxides are detected, Ru species other than **1**−**4** must be present; these are not detectable by ^{31}P NMR and could be phosphine-free and/or paramagnetic Ru(III) species.

If excess PPh_3 is added to a solution of **1** under N_2O above −40 °C, catalytic oxidation to $OPPh_3$ and formation of N_2 are evident, and phosphine oxidation is complete prior to any formation of **2**. Oxygen-atom transfer to PPh_3 from N_2O has been demonstrated previously within metal complex systems,[24] and also within a metal-free supercritical N_2O system.[6l] Attempts to oxidize olefins at ambient conditions were unsuccessful. Whether the room-temperature reaction of **1** with N_2O to give **2**, phosphine oxides, and N_2 occurs via the chemistry outlined in Figure 1 or by direct decomposition of nondetectable **3** is unclear.

The equilibrium data between precursor **1** and the N_2O adduct **3** (K_{N_2O}) and the N_2 adduct **4** (K_{N_2}) were determined in $CDCl_3$ over the temperature ranges 210−250 and 243−303 K, respectively. The relative concentrations of the species were readily measured by integration of the NMe_2 ^1H NMR signals, but there are some uncertainties in the solubility data. The K_{N_2} values are consistent using either the extrapolation of literature solubility data for $CHCl_3$ or known solubilities in acetone;[25] at 250 K, K_{N_2} is ~450 M^{-1}, with $\Delta H° = -27 \pm 3$ kJ mol^{-1} and $\Delta S° = -55 \pm 10$ J $mol^{-1}K^{-1}$ being determined from a good van't Hoff plot. Determination of the K_{N_2O} values involves a more lengthy extrapolation of solubility data in $CHCl_3$,[26] and the van't Hoff plot shows scatter, but the K_{N_2O} value at 250 K is in the range 0.4−1.0 M^{-1} (~10^3 times smaller than K_{N_2}) and this is reflected in a much lower exothermicity ($\Delta H° = -9 \pm 5$ kJ mol^{-1} and $\Delta S° = -43 \pm 25$ J $mol^{-1}K^{-1}$). The $\Delta H°$ values are a measure of the relative binding energies of the gases at Ru(II) with the ligand set shown, the conversions of **1** to **3** or **4** involving rearrangement of the Cl ligands from a trans to cis disposition; some differential scanning calorimetric measurements have shown that this process requires ~50 kJ mol^{-1},[14b] implying the Ru−N bond strengths are ~80 and 60 kJ mol^{-1} respectively for the N_2 and N_2O systems. Negative $\Delta S°$ values are consistent with the fixing of gases at a metal site. Of note, the binding of N_2 versus N_2O at the $Ru(NH_3)_5^{2+}$ moiety[12] in aqueous solution is favored by 23.4 kJ mol^{-1}, remarkably close to the relative value determined for our system. The binding strength of N_2O at Ru(II) is thus comparable to that of the N_2 ligand.

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Supporting Information Available: Crystallographic data for **2**, and van't Hoff plots for K_{N_2} and K_{N_2O} for determination of thermodynamic parameters (PDF) and CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Complex **2** may also be prepared from the reaction of **1** with O_2 or air. **2** is diamagnetic because of antiferromagnetic coupling through the Ru−Ru bond and/or the μ-oxo ligand. Green crystals of **2** were obtained by evaporation of an acetone solution of **1** in air. Crystal data for **2** ($C_{43}H_{46}Cl_4N_2O_2P_2Ru_2$): $M = 1028.75$, monoclinic, $a = 18.1176(14)$ Å, $b = 9.5777(11)$ Å, $c = 25.2917(7)$ Å, $\beta = 100.1564(7)°$, $V = 4320.0(5)$ Å^3, $T = 180$ K, space group $P2_1/a$, $Z = 4$, μ(Mo Kα) = 10.59 cm^{-1}, 39452 reflections measured, 11225 unique ($R_{int} = 0.094$), $R(I > 3\sigma(I)) = 0.055$, $R_w = 0.040$.

[18] ^1H NMR data for **3** (NMe_2 region, CD_2Cl_2, −78 °C): δ 2.95 s (3H); 3.65 s (3H). $^{31}P\{^1H\}$ NMR (wrt 85% aq H_3PO_4): $P_A = \delta$ 49.1 d, $P_X = \delta$ 39.6 d ($^2J_{pp} = 28.1$ Hz). ^{15}N NMR (wrt $^{15}NH_3$ using $Me^{15}NO_2$ in CD_2Cl_2): δ 125.8 br s; for free ^{15}NNO, δ 151.6 (br t, $J(^{15}N^{14}N) \sim 6$ Hz).

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[22] ^1H NMR data for **4** (NMe_2 region, CD_2Cl_2, −78 °C): δ 3.01 (3H), 3.60 (3H). $^{31}P\{^1H\}$ NMR (wrt 85% aq H_3PO_4): $P_A = \delta$ 47.2, $P_X = \delta$ 37.5 ($^2J_{PP} = 26.9$ Hz).

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[25] For the N_2 system, solubility data in acetone are available over the required temperature range (*IUPAC Solubility Data Series*; Kertes, A. S., Ed.; Pergamon Press: Oxford, 1982; Vol. 10, pp 216−219), while limited data from 293 to 298 K are available in $CHCl_3$ (*IUPAC Solubility Data Series*; Kertes, A. S., Ed.; Pergamon Press: Oxford, 1982; Vol. 10, pp 232−233).

[26] For the N_2O system, the required solubility data were estimated by extrapolation of literature data in $CHCl_3$ from 291 to 309 K (*IUPAC Solubility Data Series*; Kertes, A. S., Ed.; Pergamon Press: Oxford, 1981; Vol. 8, pp 220−222); at ambient conditions, N_2O is ~50 times more soluble than N_2.