Communications to the Editor

Matrix Infrared Spectra of the Osmium and Ruthenium Dinitride Molecules. Evidence for Direct Insertion of Osmium into the Dinitrogen Bond at Cryogenic Temperatures

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The dinitrogen molecule N_2 is very unreactive, and industrial nitrogen fixation requires extreme conditions to break the strong triple bond. The Haber process for the production of ammonia requires high temperatures and pressures over an iron catalyst.[1] Other metal surfaces have also been examined for effectiveness in the ammonia synthesis, including other metals in the iron group, and osmium is found to be equal to iron in its ability to promote the reaction.[2−4]

In this work, osmium and ruthenium nitrides formed by reaction of the metal atoms with dinitrogen are isolated in argon and nitrogen matrices at cryogenic temperatures. Osmium inserts directly into the dinitrogen bond during annealing in solid argon to give the bent insertion product NOsN. Ruthenium forms NRuN on deposition with energetic metal atoms, and on annealing by combination of nitrogen atoms and RuN, but there is no evidence for direct insertion of cold ruthenium atoms into the dinitrogen bond. The diatomic molecules OsN and RuN and several dinitrogen complexes are also observed, and these will be discussed in a forthcoming paper.[5]

The technique for laser ablation and matrix isolation investigation has been described previously.[6,7] Osmium (E-VAC Products, 99.98%, hot pressed) and ruthenium (Goodfellow Metals, 99.9%) metal targets were mounted on a rotating (1 rpm) stainless steel rod. The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate, 10 ns pulse width, 40−50 mJ pulses) was focused on the target through a hole in the CsI cryogenic window (maintained at 7−8 K by a Displex refrigerator). Metal atoms were co-deposited with $^{14}N_2$ and $^{14}N_2 + ^{15}N_2$ in argon (3−4%) at 5−8 mmol/h for 60−90 min, and with undiluted $^{14}N_2$ and $^{14}N_2 + ^{15}N_2$ for 30 min at the same rate. Infrared spectra were recorded with 0.5 cm^{-1} resolution on a Nicolet 550 instrument. Matrix samples were successively warmed and recooled, and more spectra were collected; the matrix was subjected to broad-band photolysis with a medium-pressure mercury arc (Philips, 175 W) with globe removed (240−580 nm) at different stages in the annealing cycles.

Figure 1 shows spectra in the 1140−860 cm^{-1} region for osmium nitride products in nitrogen and argon matrices. Figure 2 shows high-resolution spectra in the range 990−950 and 840−800 cm^{-1} for ruthenium nitride products in $^{14}N_2 + ^{15}N_2$ after annealing to 25 K.

Figure 1. Infrared spectra in the 1140−860 cm^{-1} region for laser-ablated osmium atoms co-deposited with dinitrogen: (a) after annealing to 25 K with undiluted $^{14}N_2 + ^{15}N_2$ (43% + 57% mixture), (b) after 1 h deposition with 2% $^{14}N_2$ + 2% $^{15}N_2$ in argon, (c) after annealing to 25 K, (d) after annealing to 30 K, (e) after annealing to 40 K, and (f) after annealing to 45 K. The 943 cm^{-1} band that grows on annealing is probably due to $(N_2)_xOsO_2$.
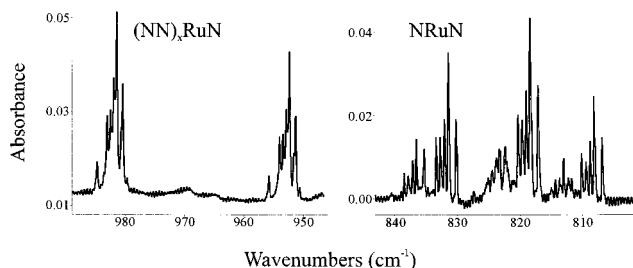
Figure 2. Infrared spectra in the 1000−950 and 840−800 cm^{-1} regions using 0.125 cm^{-1} resolution for laser-ablated ruthenium atoms co-deposited with $^{14}N_2 + ^{15}N_2$ after annealing to 25 K.

When osmium atoms are deposited with pure nitrogen, a weak band is observed at 901.2 cm^{-1} that increases on annealing and diminishes on photolysis; a less intense matrix site band at 908.3 cm^{-1} decreases on annealing but grows on photolysis. The $^{15}N_2$ counterparts for these bands at 880.4 and 873.8 cm^{-1}, respectively, give almost identical isotopic ratios of 1.03136 and 1.03169 for the two matrix sites. These are lower than the diatomic Os−N harmonic value of 1.03216 indicating a greater participation of the metal atom in this mode relative to the diatomic molecule. When the experiment is repeated using a $^{14}N_2 + ^{15}N_2$ mixture, an intermediate band is observed at 885.6 cm^{-1} with a weaker matrix site at 892.2 cm^{-1}, which are more intense than either of the pure isotopic bands (Figure 1a). The intensity pattern for this triplet of peaks is appropriate for a vibrational mode that involves two equivalent nitrogen atoms, and NOsN is the most logical assignment for these bands. The fact that the intermediate band is observed shows that the molecule is formed through reaction 1, rather than reaction 2, since no isotopically scrambled dinitrogen is present to form $^{14}NOs^{15}N$ by direct insertion. This is reasonable considering the abundance of OsN and nitrogen atoms in the pure nitrogen matrix after co-deposition with energetic laser-ablated Os atoms.[6,7]

$$OsN + N \rightarrow NOsN \tag{1}$$

$$Os + N_2 \rightarrow NOsN \tag{2}$$

Analogous bands are observed at 900.3, 884.7, and 872.9 cm^{-1} when osmium is reacted with $^{14}N_2 + ^{15}N_2$ in argon, very close to

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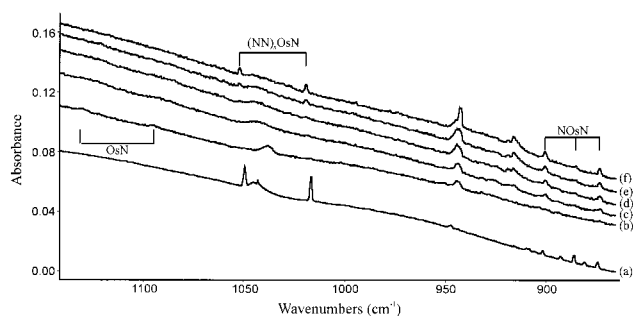
the pure nitrogen values. However, the annealing behavior for these bands in argon (Figure 1b–f) is different from that in pure nitrogen. The bands are not present initially, but grow in during annealing. The intermediate band also appears but not to the same extent, and after the final annealing cycle the intensity ratio is approximately 3:1:3. This implies that reaction 2 is dominant, but that reaction 1 is also occurring to a small extent. These observations demonstrate that cold osmium atoms insert into the dinitrogen molecule and break the strong triple bond in a cold argon matrix. This is a significant result, as it shows that the reaction *does not require activation energy and is thermodynamically favorable*. Since the temperature in the matrix is low, the entropy contribution to the free energy change is negligible. Given that the bond enthalpy in N_2 is 945 kJ/mol,[8] the average Os–N bond enthalpy in NOsN must be at least ∼473 kJ/mol. The high affinity of osmium for dinitrogen shown here parallels the high activity of the metal as a catalyst in ammonia synthesis.[4]

The 14/15 isotopic ratios of 1.03136 and 1.03115 for these bands in N_2 and N_2/Ar can be used in conjunction with the appropriate **G** matrix elements to estimate the bond angle for the bent symmetrical molecule.[9,10] If the observed bands are due to the ν_3 mode, then upper limit estimates of 120° and 126° are derived for NOsN in nitrogen and argon matrices, respectively. This is consistent with the large number of NMN molecules that have been observed with similar angles.[11–15] The isotopic ratio for the terminal atoms in the ν_3 mode of a triatomic molecule gives an upper limit for the bond angle.[9,10] The isotopic ratio for the central atom would give a lower limit on the bond angle, but unfortunately the osmium isotopes in NOsN cannot be resolved. The bands in the nitrogen matrix are sharper and their positions measured with greater accuracy, so the angle calculated using nitrogen matrix data is more accurate. Considering the results for ruthenium (see below), the best estimate for the NOsN bond angle is 115 ± 5°.

When ruthenium is co-deposited with pure $^{14}N_2$, a group of five bands is observed in the 985–980 cm^{-1} region with the natural-abundance intensity pattern for a single Ru atom and a 14/15 ratio identical with that for RuN.[5] Five new bands are also observed in the 833.4–830.2 cm^{-1} range, which correspond to the five most abundant isotopes of ruthenium; weaker matrix sites for these bands are observed in the 838.4–835.3 cm^{-1} range, analogous to the higher frequency matrix site observed for NOsN. The ^{15}N counterparts for the dominant matrix site are in the range 810.1–806.8 cm^{-1}. When the experiment is repeated with a $^{14}N_2$ + $^{15}N_2$ mixture, intermediate bands are observed in the range 820.3–817.1 cm^{-1} to give an overall intensity pattern that is appropriate for a mode that involves two equivalent nitrogen atoms (Figure 2). The straightforward assignment for these bands is to NRuN, formed by the addition of atomic nitrogen to RuN. Since the argon and nitrogen matrix frequencies are within a few

cm^{-1}, any N_2 ligation of the dinitrides apparently has a minimal effect on these frequencies.

Unlike NOsN, metal and nitrogen isotopic data are available to estimate both lower and upper limits for the NRuN bond angle, respectively.[9,10] Using both metal and nitrogen data allows lower and upper limits of 109° and 117° to be determined for the NRuN bond angle. The average value of 113 ± 5° represents a reliable estimate of the bond angle owing to cancellation of anharmonic effects. This may be compared to the 115° average angle determined for NFeN from isotopic data.[11]

Bands due to NRuN are observed in argon matrices at 831.9/830.5, 818.7/817.4, and 808.4/807.1 cm^{-1} where absorptions due to the ^{104}Ru and ^{102}Ru isotopes can be resolved. However, these bands are weak and broad, and the greater uncertainty in their positions leads to an inferior bond angle estimate compared to the nitrogen matrix data where the bands are sharp and intense. On annealing the argon matrix, the bands due to $^{14}NRu^{14}N$, $^{15}NRu^{15}N$, and $^{14}NRu^{15}N$ grow slightly but to the same degree, indicating that the molecule is formed by the addition of a nitrogen atom to RuN rather than the direct insertion of ruthenium into a dinitrogen molecule.

It could be argued that the bands assigned above to NOsN and NRuN are due to dimers of the diatomic molecules, since observation of the scrambled isotopic molecule in the mixed $^{14}N_2$ + $^{15}N_2$ experiment would be consistent with the combination of two diatomic molecules. However, this assignment must be rejected in light of the annealing behavior of the bands in the argon matrix. If a dimer were formed via the combination of OsN molecules, then a 1:2:1 intensity pattern would be observed. There is no way to reconcile the assignments of the observed bands to $(OsN)_2$ with the low intensity of the intermediate bands relative to the pure isotope bands in argon. Although growth of the analogous bands in the ruthenium nitride system on annealing is consistent with the formation of $(RuN)_2$, the resolved ruthenium isotopic data clearly show that only one ruthenium atom is present.

In summary, we have characterized the osmium and ruthenium dinitrides NOsN and NRuN by matrix infrared spectroscopy. Both molecules adopt bent geometries as estimated from the nitrogen (and ruthenium) isotopic frequency ratios. Infrared absorptions for these molecules in argon matrices are not present initially, but grow in on annealing. The strong growth of the bands due to $^{14}NOs^{14}N$ and $^{15}NOs^{15}N$ and negligible growth of the intermediate band due to $^{14}NOs^{15}N$ in the mixed $^{14}N_2$ + $^{15}N_2$ argon matrix experiments indicates that NOsN is predominantly formed by the direct insertion of osmium into the dinitrogen bond. This allows a lower limit on the average Os–N bond enthalpy in this molecule to be estimated as ∼473 kJ/mol. Such is not the case for NRuN, where growth of the NRuN bands in the mixed $^{14}N_2$ + $^{15}N_2$ argon experiment suggests that the molecule is formed by combination of nitrogen atoms and RuN molecules, rather than direct insertion of ruthenium into the dinitrogen bond. It should also be noted that cold iron atoms did not insert into dinitrogen in a previous matrix infrared study of the iron nitrides.[11]

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