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Polar Effects in Nitride Coupling Reactions

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The nucleophilic molybdenum nitride $(Et_2NCS_2)_3MoN$ (**1**) reacts with the electrophilic osmium nitride complex $TpOsNCl_2$ (**2**, Tp = hydrotris(1-pyrazolyl)borate) to produce molecular nitrogen. Reaction of **1** at the nitride is accompanied by a substantial amount of reaction at a sulfur atom of the dithiocarbamate ligand, forming the osmium thionitrosyl complex $TpOs(NS)Cl_2$ (**4**). Labeling experiments establish that the N_2 produced comes specifically (>96%) from mixed-metal (molybdenum–osmium) coupling. The major transition-metal-containing product of the reaction is the μ-nitrido complex $TpOsCl_2(\mu\text{-}N)Mo(S_2CNEt_2)_3$ (**3**), where the bridging nitride derives primarily (82%) from the osmium nitride **2**. The μ-nitrido complex **3** has been characterized crystallographically, and shows a nitride bridge that is very asymmetric (Mo–N = 1.721(3) Å, Os–N = 1.906(3) Å), with less multiple bonding toward osmium and more toward molybdenum. Heterometallic coupling is much faster than either homometallic coupling reaction, in particular the osmium–osmium coupling, despite the greater oxidizing power of osmium over molybdenum. The origin and implications of this kinetic effect on nitride coupling and dinitrogen cleavage are discussed.

Introduction

Molecular nitrogen has long exerted a strong fascination over chemists.[1] Dinitrogen is extremely abundant in the atmosphere, but its great thermodynamic stability ($D_{N\equiv N}$ = 226 kcal/mol)[2] makes it notoriously unreactive. Recently, a number of groups have succeeded in cleaving the N≡N triple bond to form well-defined transition-metal nitride complexes.[3-6] In all such reactions reported to date, nitrogen cleavage relies on highly reducing early transition metals, which form very stable nitrides. For example, the reaction of N_2 with $Mo(NRAr)_3$[3] is exothermic by 84 kcal/mol due to the very strong (155 kcal/mol) Mo≡N bond.[7] If dinitrogen cleavage requires the formation of such strong bonds, the extension of these stoichiometric reactions to catalytic processes will be extremely difficult.

Coupling of terminal metal nitrides to form dinitrogen has also been observed in a number of cases.[8-11] By the principle of microscopic reversibility, any factors that influence the kinetic facility of this reaction should also be applicable to dinitrogen cleavage. We were thus struck by the mechanistic suggestions advanced by Ware and Taube in their pioneering study of the coupling of $OsNCl_3(py)_2$ to form N_2 and $OsCl_3(py)_3$.[8] Even though this coupling involves identical nitrides,

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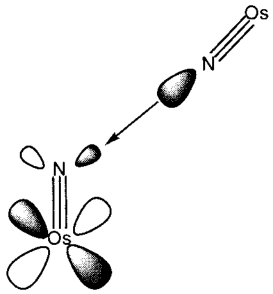

Figure 1. Proposed orbital interactions in nitride coupling (adapted from ref 8).

Ware and Taube argued that a collinear nitride−nitride approach would be unfavorable due to lone pair−lone pair repulsion. Instead, they suggested an unsymmetrical transition-state geometry[12] in which the lone pair of one nitride ligand interacts with an empty M≡N π^* orbital of another (Figure 1).

Careful consideration of this "semibent" transition state indicates that the two nitride complexes are playing quite different roles in the reaction. The complex at the upper right is acting as a nucleophile at nitrogen, and (at least initially) would not undergo a change in oxidation state. Conversely, the other nitride is acting as an electrophile, and the metal center is being reduced. Thus, what is nominally a coupling reaction might in fact be quite polar.

To further explore this hypothesis, we set out to find an example of a *hetero*metallic nitride coupling reaction. Here we describe the reaction of a nucleophilic molybdenum(VI) nitride with an electrophilic osmium(VI) nitride. The coupling reaction leads to several products, including a heterobimetallic μ-nitrido complex which has been structurally characterized. In this case heterobimetallic nitrido coupling is indeed faster than homocoupling, despite its lower thermodynamic driving force.

Experimental Section

Unless otherwise noted, all procedures were carried out on the benchtop. When necessary, methylene chloride was dried over 4 Å molecular sieves, followed by CaH_2. Dry ether was vacuum transferred from sodium benzophenone ketyl. $MoN(S_2CNEt_2)_3$ (**1**) was prepared by the method of Chatt.[13] $TpOsNCl_2$ (**2**, Tp = hydridotris(1-pyrazolyl)borate) was prepared as described by Crevier and Mayer.[14] $^{15}NH_4OH$ (Cambridge Isotope Laboratories, 98% isotopic purity) was used to prepare $KOs(^{15}N)O_3$ following a literature procedure,[15] which in turn was used to prepare $TpOs(^{15}N)Cl_2$ (**2***).[16] All other reagents were commercially available and used without further purification.

NMR spectra were measured on a Varian VXR-300 or VXR-500 or a General Electric GN-300 FT-NMR spectrometer. Chemical shifts for ^1H spectra are reported in parts per million referenced to TMS. Infrared spectra were recorded as evaporated films on KBr plates on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Mass spectra of transition-metal complexes were obtained on a JEOL JMS-AX 505HA mass spectrometer using the FAB ionization mode and 3-nitrobenzyl alcohol as a matrix. The observed intensities were in satisfactory agreement with calculated isotopic distributions. For mass spectral analysis of gaseous reaction products, a JEOL GCMate spectrometer using the EI ionization mode was employed. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ).

$TpOsCl_2(\mu\text{-}N)Mo(S_2CNEt_2)_3$ (3). To a 50 mL round-bottom flask were added a magnetic stirbar, **1** (348 mg, 0.63 mmol), and **2** (307 mg, 0.63 mmol). A Teflon needle valve was attached to the flask, which was then affixed to a vacuum line. Dry CH_2Cl_2 (10 mL) was added by vacuum transfer, and the solution stirred at 50 °C overnight. The brown solution was opened to the air and chromatographed on silica gel, eluting with CH_2Cl_2/CH_3CN (16:1). Recrystallization of the red band ($R_f = 0.51$) from benzene/ether afforded **3** as dark red crystals (127 mg, 0.12 mmol, 20%). ^1H NMR (CD_2Cl_2): δ −2.15 (br, 2H, pz); −0.15 (br, 1H, pz); 0.65 (s, 6H, CH_3); 1.44 (m, 12H, CH_3); 2.93 (br, 2H, CH_2); 3.23 (br, 2H, CH_2); 3.86 (m, 7H, $3CH_2$ + pz); 4.02 (br, 2H, CH_2); 4.86 (br, 2H, pz); 6.51 (br, 1H, pz); 6.98 (br, 2H, pz). IR (cm^{-1}): 3110 (w), 2977 (m), 2933 (m), 2873 (w), 2504 (w, ν_{BH}), 1510 (vs), 1458 (m), 1438 (s), 1405 (m), 1380 (w), 1357 (m), 1312 (w), 1275 (s), 1211 (s), 1148 (m), 1116 (w), 1075 (w), 1049 (s), 1016 (w), 915 (w), 849 (w), 790 (w), 762 (m), 709 (m). FABMS: *m/z* 1029 (M^+). Anal. Calcd for $C_{24}H_{40}N_{10}S_6BCl_2OsMo$: C, 28.02; H, 3.92; N, 13.61. Found: C, 28.47; H, 4.29; N, 13.44.

$TpOsCl_2(\mu\text{-}^{15}N)Mo(S_2CNEt_2)_3$ (3*). This complex was prepared by the same method with **2*** as the starting material. Least-squares fitting of the isotope envelope observed by FABMS shows that the product is 82 ± 1% labeled; *m/z* 1030 (M^+).

Homocoupling Reactions. To a screw-cap NMR tube was added **1** (20 mg, 36 μmol), and to another tube was added **2** (20 mg, 41 μmol). Approximately 0.5 mL of CD_2Cl_2 was added to each tube. The tubes were capped and subsequently monitored by ^1H NMR spectroscopy. The tubes were heated by immersion in a 50 °C oil bath. Reaction progress was monitored for 1 week.

Time Course of Heterocoupling. To a 50 mL Erlenmeyer flask were added **1** (27.8 mg, 0.05 mmol), **2** (24.5 mg, 0.05 mmol), and dimethyl terephthalate (1 mg, internal standard). A syringe was used to add 2 mL of CD_2Cl_2. The flask was swirled briefly to dissolve the reagents, and then a syringe was used to transfer a 0.5 mL aliquot of the dichloromethane solution to each of three screw-cap NMR tubes. The tubes were sealed and subsequently monitored by ^1H NMR spectroscopy for 9 h. The tubes were heated by immersion in a 50 °C oil bath. Reaction progress was monitored by integration relative to the δ 8.08 peak of dimethyl terephthalate, and yields reported are the average of all three tubes.

Dinitrogen Analysis. A gas-sampling apparatus was constructed by attaching a 7 cm copper tube with a Swagelok fitting to a glass side arm with a Teflon needle valve on the side of a 10 mL round-bottom flask. In a typical experiment, **1** (96.8 mg, 0.20 mmol), **2*** (107.3 mg, 0.20 mmol), and a magnetic stirbar were placed at the bottom of the modified round-bottom flask. A needle valve with a standard taper joint was attached, and the entire apparatus was affixed to a vacuum line. Dry CH_2Cl_2 (4 mL) was added by vacuum transfer, the needle valve closed, and the solution heated in a 50 °C oil bath for 17 h. The Swagelok fitting was plumbed to the

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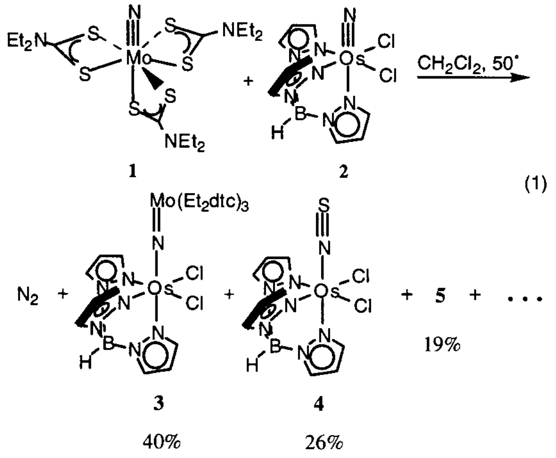
inlet of the mass spectrometer. The 10 mL flask was cooled in liquid nitrogen, and with the needle valve still closed the entire system was evacuated for 5 min. The side arm needle valve was then opened, and the headspace of the gas sampling apparatus was analyzed using EI-MS.

X-ray Structure Determination of $TpOsCl_2(\mu\text{-}N)Mo(S_2CNEt_2)_3 \cdot C_6H_6$ ($3 \cdot C_6H_6$). Red plates of the complex were deposited after slow diffusion of ether into a solution of **3** in benzene. A 0.35 × 0.15 × 0.08 mm crystal was glued to the tip of a glass fiber in the air and examined at 20 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation with a graphite monochromator (λ = 0.71073 Å). The crystal was triclinic, and the space group was identified as $P\bar{1}$. The unit cell was determined on the basis of 25 reflections with $13.8° < \theta < 15.3°$. Crystal quality was monitored by recording three standard reflections approximately every 180 reflections measured; decay was negligible. An empirical absorption correction was applied (μ = 3.734 mm^{-1}, transmission factors 0.4336−0.5699). The osmium and molybdenum atoms were located on a Patterson map. The remaining non-hydrogen atoms were found by difference Fourier syntheses. Hydrogens in the complex were placed in calculated positions. Final full-matrix least-squares refinement on F^2 converged at R1 = 0.0268 for 6605 reflections with $F_o > 4\sigma(F_o)$ and R1 = 0.0340 for all data (wR2 = 0.0630 and 0.0663, respectively.). All calculations used SHELXTL (Bruker Analytical X-ray Systems), with scattering factors and anomalous dispersion terms taken from the literature.[17]

Results

Two electronically dissimilar metal nitrides were chosen for attempted heterocoupling. The molybdenum(VI) nitrido complex $(Et_2NCS_2)_3MoN$ (**1**) was first prepared by Chatt and co-workers.[13] The electron-releasing dithiocarbamate ligands are believed to enhance the nucleophilicity of the nitride ligand,[18] which reacts with a variety of organic electrophiles.[19] In contrast, the osmium(VI) nitride complex $TpOsNCl_2$ (**2**), prepared by the Mayer group several years ago, has been shown to react with nucleophilic reagents.[14,16,20,21] Both nitride complexes are relatively stable by themselves. Molybdenum complex **1** is unchanged after being heated for 7 d at 50 °C in CD_2Cl_2. The osmium nitride complex **2** does decompose into paramagnetic products under these conditions, but very slowly (75% decomposed after 7 d).

In contrast, heating **1** and **2** together at 50 °C in dichloromethane causes relatively rapid disappearance of the metal nitrides. Monitoring by ^{1}H NMR indicates that the osmium nitride **2** is largely consumed within 3 h and completely gone after 20 h. (The disappearance of the molybdenum nitride **1** cannot be followed accurately by ^{1}H NMR in this reaction because of the complexity of the spectrum in the region where the ethyl signals are observed.) The reaction forms N_2 and several osmium-containing byproducts (eq 1; yields based on $TpOsNCl_2$).



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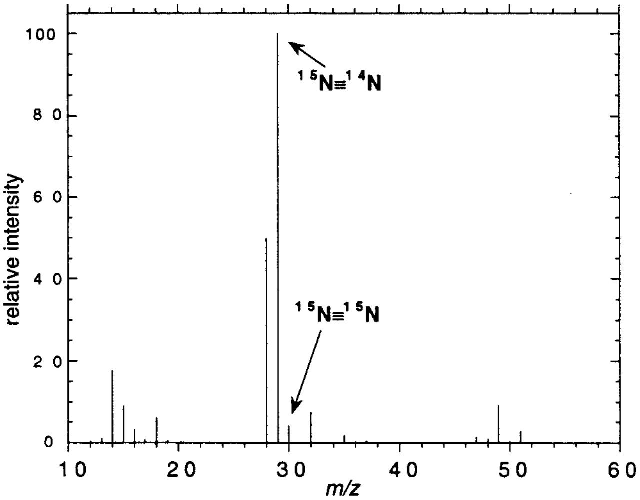

Figure 2. Mass spectrum of the headspace of the reaction mixture after heating of **1** and **2*** for 17 h at 50 °C in CH_2Cl_2.

Gaseous N_2 was detected by mass spectrometric analysis of the headspace of the reaction vessel. To verify that dinitrogen is formed in a heterocoupling process, the ^{15}N-labeled Os(VI) complex $TpOs(^{15}N)Cl_2$ (**2***) was used. Heterocoupling was confirmed by the strong signal for $^{15}N^{14}N$ at m/z = 29 in the mass spectrum (Figure 2). A signal for doubly labeled $^{15}N_2$ at m/z = 30 was barely detectable (<4% relative intensity), which confirms that homonuclear Os(VI)−Os(VI) coupling is not a significant process over the duration of the experiment. The signal for unlabeled N_2 at m/z = 28 is almost certainly due to slight leakage of air into the apparatus or spectrometer, as judged by the presence of a corresponding peak due to O_2 at m/z = 32.

A mixture of metal-containing products was observed in the ^{1}H NMR spectrum of the reaction solution. The three tris(pyrazolyl)borate-containing products **3**−**5** together account for 85% of the **2** initially present, on the basis of NMR integration relative to an internal standard. The major osmium-containing compound is a red paramagnetic complex, **3**, which could be isolated from the reaction mixture by column chromatography on silica gel. The IR spectrum of **3** shows bands which are indicative of dithiocarbamates (1508 cm^{-1}, ν_{CN}) as well as a B−H stretch at 2504 cm^{-1}, suggesting that **3** contains both osmium and molybdenum.

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Table 1. Crystallographic Data for **3**·C_6H_6

empirical formula	$C_{30}H_{46}BCl_2MoN_{10}OsS_6$	α (deg)	74.706(12)
fw	1106.98	β (deg)	88.109(11)
temp (K)	293	γ (deg)	70.697(11)
λ	0.71073 Å (Mo Kα)	V (Å$^{3)}$	2127.9(5)
space group	$P\bar{1}$	Z	2
total no. of data collected	7474	calcd ρ (g/cm^3)	1.728
no. of indep reflns	7474	cryst size (mm)	0.35 × 0.15 × 0.08
a (Å)	11.885(2)	μ (mm^{-1})	3.734
b (Å)	12.372(2)	R indices [$I > 4\sigma(I)$]^a	R1 = 0.0268, wR2 = 0.0630
c (Å)	15.924(2)	R indices (all data)^a	R1 = 0.0340, wR2 = 0.0663

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2)^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**·C_6H_6

Os−N1	1.906(3)	Mo−S4	2.4798(11)
Os−N32	2.046(3)	Mo−S2	2.5090(11)
Os−N22	2.056(3)	Mo−S6	2.5102(12)
Os−N12	2.103(3)	Mo−S5	2.5177(11)
Os−Cl2	2.3489(11)	Mo−S1	2.5277(11)
Os−Cl-1	2.3587(11)	Mo−S3	2.6643(11)
Mo−N1	1.721(3)		
N1−Os−N32	93.11(13)	N12−Os−Cl2	90.58(10)
N1−Os−N22	92.26(13)	N1−Os−Cl1	90.50(9)
N32−Os−N22	87.33(13)	N32−Os−Cl1	89.82(10)
N1−Os−N12	177.41(13)	N22−Os−Cl1	176.13(9)
N32−Os−N12	84.74(13)	N12−Os−Cl1	90.94(10)
N22−Os−N12	86.20(13)	Cl2−Os−Cl1	93.37(4)
N1−Os−Cl2	91.48(9)	Mo−N1−Os	173.7(2)
N32−Os−Cl2	174.39(9)	C13−N12−Os	133.9(2)
N22−Os−Cl2	89.27(10)	N11−N12−Os	119.7(2)

The ^{1}H NMR displays somewhat broadened peaks which are paramagnetically shifted. The dithiocarbamato methyl resonances appear at δ 0.65 (6H) and δ 1.44 (12H), and the methylene resonances appear at δ 2.93, 3.23, 3.86, and 4.02 in a 2:2:6:2 ratio. The number and relative intensities of the dithiocarbamato resonances are consistent with a nonfluxional molecule possessing C_s symmetry, albeit with some accidental degeneracies. The pyrazole resonances are broad and widely dispersed (range δ −2.15 to +6.98) and again are consistent with C_s symmetry. FABMS shows a peak at m/z 1029, consistent with the formula $TpOsCl_2(N)Mo(S_2CNEt_2)_3$; the isotope pattern is consistent with a bimetallic species containing one Os atom, one Mo atom, one B atom, and two Cl atoms. When the coupling reaction is carried out with the isotopically labeled compound **2***, FABMS shows that the μ-nitrido complex **3*** obtained is 82 ± 1% enriched in ^{15}N.

A single-crystal X-ray diffraction study of **3**, as its benzene solvate, indicates that the complex is a heterobimetallic μ-nitrido complex, $TpOsCl_2(\mu\text{-}N)Mo(S_2CNEt_2)_3$, where the two metal centers are linked by an unsupported nitride bridge. Crystal data are summarized in Table 1, and selected bond distances and angles are presented in Table 2. As can be seen from Figure 3, the compound contains an octahedral osmium fragment and a pentagonal bipyramidal molybdenum fragment bridged by a nitride. The Os−N−Mo linkage is nearly linear (173.7(2)°), which is typical of unconstrained bridging nitrides.[22] The Mo−N distance (1.721(3) Å) is nearly as short as in the terminal nitride **1** (1.641(9) Å).[23]

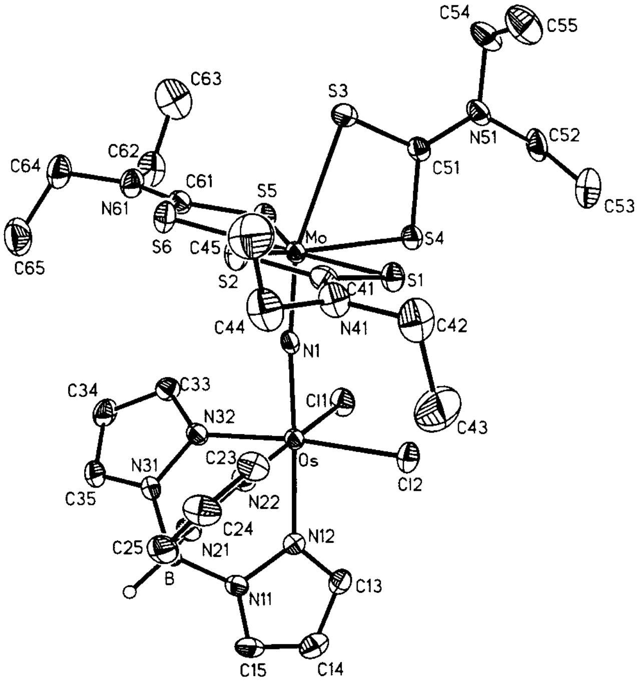

Figure 3. SHELXTL plot (30% thermal ellipsoids) of **3**.

The Os−nitrido distance of 1.906(3) Å is substantially shorter than a single bond (compare the Os−pyrazole distances of 2.046−2.103 Å in **3**).

Two other osmium-containing products are apparent in ^{1}H NMR spectra of the crude reaction mixture. The known green thionitrosyl complex $TpOs(NS)Cl_2$ (**4**)[16] could be isolated from the mixture by chromatography and was identified by ^{1}H NMR spectroscopy and FAB mass spectrometry. This complex, which is observed in 26% yield by NMR in the crude reaction mixture, most likely results from the desulfurization of a dithiocarbamate ligand of **1** by the osmium nitride **2**. Desulfurization of dithiocarbamates is well-precedented.[24] Reaction with ^{15}N-labeled **2*** gives the thionitrosyl $TpOs(^{15}NS)Cl_2$ (**4***) with complete ^{15}N enrichment as judged by FABMS. The final TpOs-containing product, **5**, has two pyrazole triplets at δ 6.01 and 6.09 (2:1 ratio, J = 2 Hz), and four doublets at δ 7.24, 7.51, 7.54, and 7.75 (2:

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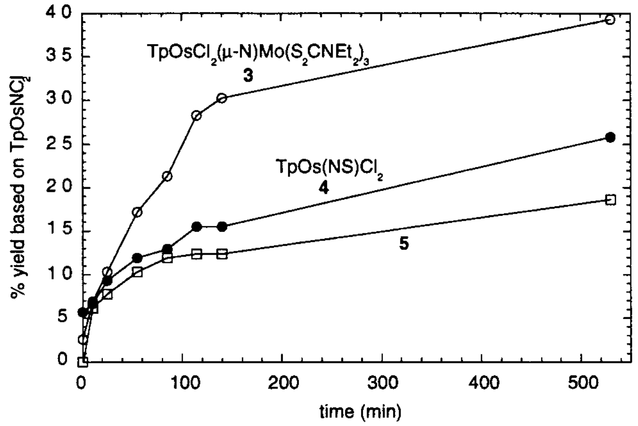

Figure 4. Yield, based on TpOsNCl$_2$, of **3** (open circles), **4** (solid circles), and **5** (open squares) in the reaction of **1** with **2** at 50 °C in CD$_2$Cl$_2$.

1:2:1 ratio, $J = 2$ Hz), which indicate that the species is diamagnetic and possesses mirror symmetry. This species decomposed upon chromatography on silica gel and could not be isolated or further characterized.

The time evolution of the coupling reaction at 50 °C in CD$_2$Cl$_2$ (eq 1) was examined by integration of the resonances of **3**−**5** in the ^{1}H NMR against an internal standard (Figure 4). It is clear that the formation of the three major products begins immediately with no induction period. This suggests that the species are formed by independent, rather than consecutive, pathways. Complex **2** is approximately 50% consumed after 90 min.

Discussion

Structure and Bonding of TpOsCl$_2$(μ-N)Mo(S$_2$CNEt$_2$)$_3$ (3). Loss of N$_2$ from **1** and **2** is a net reduction and would be expected to generate coordinatively unsaturated molybdenum- and osmium-containing fragments. Binding of unreacted metal nitrido complex to these fragments would generate the μ-nitrido complex **3**, which is observed in 40% yield. Such "incomplete atom transfer"[25] reactions of terminal nitrides with labile or coordinatively unsaturated metal centers are the most common method of preparing heterobimetallic μ-nitrido complexes,[26−30] although silylimido complexes have also been used as precursors.[31] In almost all crystallographically characterized compounds, the bonding is strongly asymmetric and is well-described as M≡N−M′, with N−M′ $\gtrsim$ 2.0 Å.[26−28,31] The only reported exceptions are in μ-nitrido complexes of **2**, where short N−M′ bonds have been attributed to back-bonding to a π-acidic Os≡N moiety.[30]

Since the μ-nitrido complex **3** is the first reported heterobimetallic nitride-bridged complex in which both metal fragments are known to support a terminal nitride group, one might expect the competition for π-bonding to the nitride in **3** to be more evenly matched between osmium and molybdenum than has been observed in previous complexes. Indeed, the metrical data from the crystal structure of **3** indicate that while the bonding is quite asymmetrical, both metals have significant multiple bonding toward the nitride. The observed Mo−N distance (1.721(3) Å) indicates substantial multiple bonding to molybdenum. This bond is about 0.08 Å longer than the terminal nitride distance in **1**.[23] The fact that bond distances in formally triply bonded imido complexes such as [(Me$_2$NCS$_2$)$_3$Mo(NCPh$_3$)]$^+$ (Mo−N = 1.731 (2) Å)[19] and in formally doubly bonded diazenido complexes such as (Me$_2$NCS$_2$)$_3$Mo(NNCO$_2$Et) (Mo−N = 1.732(5) Å)[32] are so similar makes the Mo−N distance observed in **3** less useful for more detailed assignment of the bonding,[33] although it is clear that the bond order is somewhere between 2 and 3. The Os−N distance in **3** (1.906(3) Å) is much longer than an OsN triple bond (∼1.65 Å) and somewhat larger than the OsN double bonds in the symmetrical μ-nitrido complex Os$_2$N(S$_2$CNMe$_2$)$_5$ (Os−N = 1.76 Å)[34] or in azavinylidene complexes (1.81−1.88 Å).[35,36] Nevertheless, the OsN distance in **3** is much shorter than expected for a single bond. The Os−N distance in **3** is strongly reminiscent of the 1.90 Å distances between the central Os and the bridging nitrides in the mixed-valence trimers [Cl$_3$(4-RC$_5$H$_4$N)$_2$Os(μ-N)]$_2$OsCl$_2$(4-RC$_5$H$_4$N)$_2$ (R = Et, ^{t}Bu), where a qualitative MO analysis indicates an Os−N bond order of 1.5 although the authors suggest there may be somewhat less bonding than this.[11] The molybdenum clearly dominates the π-bonding in **3**, but the osmium−nitrogen bond retains significant multiple bonding. The bonding is more symmetrical than in previously reported heterobimetallics, and approaches the situation in the homometallic, but asymmetrically ligated, (^{t}BuPhN)$_3$Mo(μ-N)-Mo(SAd)$_3$ (Mo−N = 1.771(7) and 1.882(7) Å).[37]

The delocalized but unsymmetrical bonding in **3** can be rationalized by considering the molecular orbitals involved (Figure 5). For a symmetric μ-nitride, the six π orbitals split into a bonding, a nonbonding, and an antibonding set.[38] If two metal centers of different electronegativities are involved, energy considerations dictate that the more electronegative

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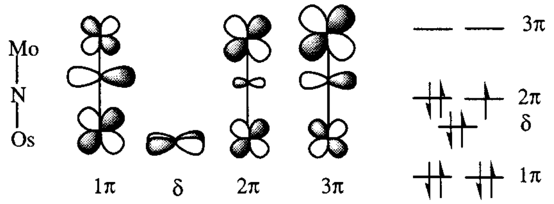
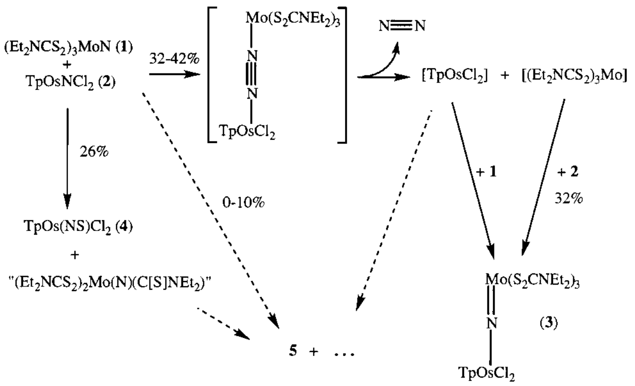


Figure 5. Qualitative description of bonding in **3**.

Scheme 1. Possible Pathways in the Reaction of **1** and **2**[a]



[a] Percentages listed reflect the fraction of the osmium complex **2** consumed on the indicated paths.

metal (here, Os) will contribute more to the lower-lying orbitals and the more electropositive metal (here, Mo) will contribute more to the higher-lying orbitals. The loss of symmetry means that the 2π orbitals, strictly nonbonding in the symmetrical μ-nitride, will become somewhat antibonding with respect to the more electronegative element. Thus, in "electron-poor" heterobimetallics with the 2π levels empty (e.g., $(MeCp)_2ZrCl(\mu\text{-}N)V(NPh_2)$[28]), the more electronegative element bonds more strongly to nitrogen, while in "electron-rich" complexes with the 2π levels filled (e.g., $(Me_3SiO)_3V(\mu\text{-}N)PtMe(PEt_3)_2$[31a]), it is the more electropositive element that has the short M−N bond. In **3**, the 2π levels are three-quarters filled, and the more electropositive molybdenum forms the shorter bond to nitrogen. The complex nominally has an orbitally degenerate ground state, but (possibly because the low true symmetry lifts the orbital degeneracies) any Jahn−Teller distortions (such as the very slightly bent nitride bridge, Mo−N−Os = 173.7(2)°) are small.

Reaction Pathways between $(Et_2NCS_2)_3MoN$ and $TpOsNCl_2$. The molybdenum complex **1** and the osmium nitride complex **2** react with each other much more rapidly than either nitride reacts with itself. Understanding this reaction in detail is hampered by the system's complexity (>3 osmium-containing materials are formed), by difficulties in monitoring the fate of the molybdenum complex, and by limits on our ability to track (15% of NMR-silent material) and characterize (19% yield of **5**) the osmium-containing products. Despite these important limitations, a number of key features of the reaction pathways between **1** and **2** are apparent and are summarized in Scheme 1.

One important conclusion is that heterometallic nitride coupling takes place, as indicated by the nearly exclusive formation of $^{15}N{\equiv}^{14}N$ (>20:1 relative to $^{15}N^{15}N$) from **1** and **2***. A plausible intermediate in forming N_2 is the unobserved heterobimetallic μ-N_2 complex $TpOsCl_2(\mu\text{-}N_2)Mo(S_2CNEt_2)_3$ depicted in Scheme 1, but in any case loss of N_2 from **1** + **2** would form the unsaturated fragments $[TpOsCl_2]$ and $[Mo(S_2CNEt_2)_3]$. Combination of the former with the molybdenum nitride **1**, or the latter with osmium nitride **2**, would form the mixed-metal nitride-bridged complex **3**, which accounts for 40% of the osmium initially present. Labeling experiments show that **3***, formed from **1** and **2***, is 82 ± 1% enriched in ^{15}N, so the Mo(III)/Os(VI) reaction is the major pathway for formation of the bridging nitride. Though it is superficially surprising that the less nucleophilic osmium nitride should react more efficiently as a ligand, in fact coordination of the nitride involves considerable reduction at osmium, and the osmium nitride **2** is quite reactive toward inner-sphere reductants. Overall, reaction with molybdenum(III) accounts for 32% of the consumption of $TpOsNCl_2$. Since the Mo(III) fragment is formed by nitrogen abstraction from $(Et_2NCS_2)MoN$, then this indicates that *at least* 32% of the $TpOsNCl_2$ must be consumed directly by nitride coupling as well.

Another major pathway that consumes $TpOsNCl_2$ produces the thionitrosyl complex **4**, formed in 26% yield. Formation of **4** appears to result from the direct reaction of osmium nitride **2** with molybdenum nitride **1** by a pathway that is independent of nitride coupling. The thionitrosyl **4** and μ-nitride complex **3** are formed more or less concurrently (Figure 1). If anything, thionitrosyl formation is somewhat faster than μ-nitride formation in the early stages of the reaction, suggesting that the source of sulfur is probably **1** rather than some byproduct of **1** formed during the coupling reaction. Desulfurization of $(Et_2NCS_2)_3MoN$ cannot initiate nitride coupling, since the $(Et_2NCS_2)_3Mo$ fragment in **3** is intact, and the yield of **3** derived from molybdenum(III) exceeds the yield of $TpOs(NS)Cl_2$. Similarly, it is difficult to see how formation of $[TpOsCl_2]$ could mediate formation of the osmium thionitrosyl **4**, especially since labeling studies show that the thionitrosyl nitrogen is derived from the osmium nitride **2**.

In summary, the observed yields indicate that three pathways—denitrification of $TpOsNCl_2$, trapping of $TpOsNCl_2$ by Mo(III), and sulfurization of $TpOsNCl_2$ by $(Et_2NCS_2)_3MoN$—account for at least 90% of the consumption of $TpOsNCl_2$. The remaining 10% might be consumed by nitride coupling (if trapping of $[(Et_2NCS_2)_3Mo]$ by **2** is not completely efficient), or by other pathways. In any case, it is apparent that $TpOsNCl_2$ reacts with $(Et_2NCS_2)_3MoN$ predominantly by attack at either nitrogen or sulfur, with a modest preference for the former (32−42% vs 26%).

Importance of Polar Effects on Nitride Coupling. There are a number of examples in the literature that support the notion that asymmetry may accelerate nitride coupling. The clearest case is that described by Che and co-workers,[9] who showed that the unsymmetrical coupling reaction between the metastable complex $[Os^{V}N(NH_3)_4]^{2+}$ (prepared in situ by photoinduced electron transfer) and $[Os^{VI}N(NH_3)_4]^{3+}$ occurs very rapidly ($k_2 = 3.75(30) \times 10^5$ M^{-1} s^{-1}) to produce the mixed-valence complex $[(MeCN)Os(NH_3)_4(\mu\text{-}N_2)Os(NH_3)_4(NCMe)]^{5+}$. The Os(V)−Os(VI) cross-coupling is much faster than the symmetrical Os(VI)−Os(VI) homocoupling reaction (the osmium(VI) nitride is stable in solution). In this case, the observed kinetics rule out consumption of the Os(V) transient by self-coupling. Similarly, Meyer has reported that the chemical or electrochemical reduction of a variety of osmium(VI) nitrides induces very efficient nitride coupling to form N_2-bridged complexes.[10] By analogy with the Che study, this may plausibly be attributed to rapid Os(V)−Os(VI) coupling (followed by reduction of the Os(III)−Os(II) dimer to the observed Os(II)−Os(II) product), although the electrochemical data do not exclude the possibility of dimerization of Os(V) transients. Enhancement of dinitrogen cleavage, the microscopic reverse of nitrido coupling, on desymmetrization has also been observed in one case. Cummins has shown that the heterobimetallic species $[(Ar[^tBu]N)_3Mo(\mu\text{-}N_2)Nb(N[^iPr]Ar)_3]^-$, generated electrochemically from its neutral precursor, decomposes into nitrido fragments before a return wave can be generated in the cyclic voltammogram.[5] This reaction is much faster than cleavage of the isoelectronic $Mo(\mu\text{-}N_2)Mo$ dimer, which has a half-life of about 30 min at room temperature.[3]

Unfortunately, the above observations suffer from a fundamental ambiguity. Addition of an electron to Os(VI)≡N populates an osmium−nitrogen antibonding orbital and strongly destabilizes the nitride, so denitrification of osmium(V) will be much more favorable thermodynamically than denitrification of osmium(VI). Likewise, because Nb(II) is much more reducing than Mo(III), its oxidation by N_2 will be correspondingly favored thermodynamically. Thus, it is unclear in the above reactions whether the observed accelerations reflect a specific stabilization of the transition state in the unsymmetric reactions or simply their enhanced thermodynamic driving forces. We thus sought a system where we could examine an unsymmetric nitride coupling reaction that would be *less* thermodynamically favorable than homocoupling.

The complexes **1** and **2** proved to be an ideal nucleophile−electrophile pair for the heteronuclear coupling reaction. In particular, the osmium(VI) nitride is much more easily reduced than the molybdenum(VI) nitride. For example, **2**[39] and many other osmium nitrides[40] react rapidly with phosphines to form osmium(IV) phosphiniminato complexes, while we find that **1** is inert to phosphines such as PMe_2Ph over several days at room temperature. Since Mo(VI) is a much poorer oxidant than Os(VI), the thermodynamic driving force for the Os(VI)−Os(VI) homocoupling reaction should be greater than that for the Mo(VI)−Os(VI) heterocoupling reaction (and much greater than that for Mo(VI)−Mo(VI) coupling). The relative amounts of $^{15}N{\equiv}^{14}N$ and $^{15}N{\equiv}^{15}N$ obtained in the gas sampling experiment indicate that, despite its lower driving force, the Mo(VI) nitride **1** undergoes coupling with osmium(VI) nitride **2** at least 20 times faster than the latter compound self-couples. A similar effect is seen in comparing gross rates of decomposition, in that the Os(VI)−Mo(VI) cross-reaction proceeds about 20 times faster than the Os(VI)−Os(VI) self-reaction (hours vs days at 50 °C in CD_2Cl_2). However, this latter experiment is more difficult to interpret quantitatively, since only about a third of the Os(VI) is consumed by nitride coupling in the former reaction, and an unknown amount in the latter. Qualitatively, though, both measures indicate that there is a significant rate acceleration in the coupling of $Mo^{VI}N$ with $Os^{VI}N$ over coupling of $Os^{VI}N$ with $Os^{VI}N$ despite the unquestioned superiority of osmium(VI) over molybdenum(VI) as an oxidizing agent. In this case, enhancement of the coupling process must therefore be a purely kinetic effect, not a thermodynamic one.

Since complexes **1** and **2** are extremely inert to ligand substitution, it is almost certain that nitride coupling takes place by direct interaction of the nitride ligands with each other, without prior coordination of one nitride to the other metal center. Given the characteristic nucleophilic behavior of $(Et_2NCS_2)_3MoN$ and the characteristic electrophilic behavior of $TpOsNCl_2$, it seems likely that the observed rate enhancement of **1** reacting with **2** is due to the enhanced ability of **1** to act as a nucleophile attacking electrophilic **2**; $TpOsNCl_2$ itself is an exceedingly feeble nucleophile.[30] This is in excellent agreement with the semibent transition state of Ware and Taube (Figure 1),[8,12] where the disparate reactivity of the two nitrides fit them well to serve the disparate roles in the coupling reaction, and lends credence to the view that this "coupling" reaction might be intrinsically polar. However, the observation of rate accelerations on polarizing the nitride coupling reaction does not prove that the transition state is unsymmetrical (note that recent theoretical analyses of (symmetric) dinitrogen cleavage reactions have favored symmetrical, "zigzag" transition states).[3b,41,42] It is well-known that the introduction of polar effects in otherwise nonpolar reactions such as radical abstractions or additions can effect substantial rate accelerations.[43] This study demonstrates the efficacy of polar effects in lowering the barrier to nitride coupling, regardless of whether it is due to better matching of an intrinsically polar reaction, or to the beneficial introduction of polar character to an otherwise nonpolar one. The principle of microscopic reversibility dictates that introducing polar effects should be effective in reducing the kinetic barriers in dinitrogen cleavage as well, and may be a useful tool to bring us closer to catalytic activation of this important and challenging substrate.

Conclusions

The nitrido complexes **1** and **2** couple to form dinitrogen under mild conditions. Heterobimetallic coupling is much

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faster than homocoupling, despite its lower driving force. Therefore, the rate acceleration is a kinetic effect, and is attributed to a favorable polarization of the transition state between the nucleophilic molybdenum nitride and the electrophilic osmium nitride. A structural analysis of the major metal-containing product **3** shows a nearly linear Os−N−Mo unit with considerable π-bonding to both transition-metal centers, but much more to the Mo center (Mo−N = 1.721(3) Å; Os−N = 1.906(3) Å).

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Supporting Information Available: Tables of crystallographic parameters, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates for **3**·C_6H_6 and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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