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Kinetic Effects in Heterometallic Dinitrogen Cleavage

Sean B. Seymore and Seth N. Brown*

Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall,
University of Notre Dame, Notre Dame, Indiana 46556-5670

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The rhenium(I) dinitrogen complex $(PhMe_2P)_4ClRe(N_2)$ reacts with $[Mo_2(S_2CNEt_2)_6](OTf)_2$ (**6**) to give the N_2-bridged complex $[(PhMe_2P)_4ClRe(\mu\text{-}N_2)Mo(S_2CNEt_2)_3]OTf$ ([**7**]OTf). Spectroscopic (ν_{NN} = 1818 cm^{-1}) and structural data [d_{NN} = 1.167(6) Å] indicate that the bridging N_2 moiety in $\mathbf{7}^+$ is slightly activated relative to free N_2 or to the mononuclear Re complex. However, the complex is stable with respect to N_2 cleavage. The putative products of such a cleavage, the known $(Et_2NCS_2)_3Mo(N)$ (**5**) and the newly prepared $[(PhMe_2P)_4ClRe(N)]OTf$ ([**9**]OTf), are stable compounds that do not react with each other to give products of nitride coupling. Thus, the failure of $\mathbf{7}^+$ to interconvert with **5** and $\mathbf{9}^+$ is due not to the thermodynamic stability of the $N\equiv N$ bond but rather to kinetic factors that disfavor N_2 cleavage and nitride coupling. Implications of this result for using polar effects to facilitate N_2 cleavage to nitrides as a strategy for nitrogen fixation are discussed.

Introduction

The legendary inertness of N_2, and the enormous practical importance of encouraging it to react, has spurred the development of its coordination chemistry.[1] The inertness of N_2 is generally ascribed to its great thermodynamic stability. Nevertheless, over the past decade or so, a number of reactions of N_2 have been discovered in which the strong $N\equiv N$ bond is cleaved spontaneously to form two equivalent[2] or different[3] metal−nitrogen multiple bonds. In these reactions, the extremely strong metal−nitrogen bonds formed by the electropositive early transition metals used in these reactions provide the driving force needed to cleave the $N\equiv N$ bond. However, this very driving force poses challenges to making these systems competent in catalytic reactions because these bonds must break to achieve turnover. Thus, while catalysis with synthetic monometallic systems using sequential proton and electron transfer to reduce N_2 has recently been achieved,[4] catalytic cycles based on N_2 cleavage to nitrides have not yet been demonstrated.

In a study of the microscopic reverse of N_2 cleavage, nitride coupling, we found that the osmium nitride complex $TpOs(N)Cl_2$ reacted with the molybdenum nitride complex $(R_2NCS_2)_3Mo(N)$ much more rapidly than either nitride underwent self-coupling.[5] The rate acceleration was attributed to the introduction of a polar effect into the coupling reaction, with the molybdenum nitride having nucleophilic character and the osmium nitride having electrophilic character. This result suggested the intriguing possibility that polar effects should lower the barrier for N_2 cleavage as well, perhaps allowing the participating metals to be shifted to the right in the periodic table. Such a shift would increase the reactivity

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* To whom correspondence should be addressed. E-mail: Seth.N.Brown.114@nd.edu.

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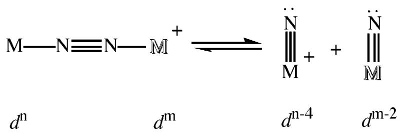
of the product nitrides[6] and enhance the possibility of achieving catalysis. In particular, we were intrigued by the possibility of a fundamentally unsymmetrical nitride cleavage reaction, where the six electrons needed to reduce N_2 were apportioned unequally, with one metal center being oxidized by four electrons and the other by two (eq 1). This would constitute a formal heterolysis of N_2 into "N^+" and "N^-" fragments.



$$\underset{d^n}{M}-N{\equiv}N-\underset{d^m}{\mathbb{M}}^{+} \rightleftharpoons \underset{d^{n-4}}{M{\equiv}\ddot{N}^{+}} + \underset{d^{m-2}}{\mathbb{M}{\equiv}\ddot{N}} \qquad (1)$$

Here we describe the reactivity of some rhenium(I) dinitrogen complexes with $[Mo_2(S_2CNEt_2)_6](OTf)_2$ (**6**), which has previously been shown to act as a source of the $[Mo(S_2CNEt_2)_3]^+$ fragment.[7] Chatt[8] and others[9] have demonstrated that rhenium(I) dinitrogen complexes such as $(PhMe_2P)_4Re(N_2)Cl$ (**1**) will react with Lewis acids to form bridged adducts. Two-electron oxidation of the Mo fragment with concomitant transfer of one N atom (formal abstraction of "N^-") in such a bridged complex would potentially form the known d^0 nitride $(Et_2NCS_2)_3Mo(N)$ (**5**),[10] as well as a cationic rhenium(V) nitrido complex. Thus, oxidation of the metal fragments (Re by 4e and Mo by 2e) to the metal nitrides could potentially provide the six electrons required to cleave N_2 (eq 1). In fact, the bridging N_2 complexes do not cleave to form nitrides, and the nitrides do not couple to form N_2 complexes. We conclude that kinetic, not thermodynamic, factors govern the stability of N_2 in this system. These results highlight the challenges involved in generating a sufficiently electrophilic N acceptor in a system that is thermodynamically able to reduce N_2.

Experimental Section

General Methods. Unless otherwise noted, all procedures were carried out on the benchtop. When necessary, chloroform and methylene chloride were dried over 4-Å molecular sieves, followed by CaH_2. Acetone was dried over 4-Å molecular sieves. Benzene was dried over sodium and ether over sodium benzophenone ketyl. $(PhMe_2P)_4Re(N_2)Cl$ (**1**),[11] $(PhMe_2P)_3Re(N_2)(S_2CNEt_2)$ (**2**),[12] $(dppe)_2Re(N_2)Cl$ (**3**),[13] $(dcpe)_2Re(N_2)Cl$ (**4**),[13] $(PhMe_2P)_3Re(N)Cl_2$,[14] $[(dppe)_2Re(N)Cl]Cl$,[15] $(Ph_3P)_2Re(N)Cl_2$,[16] $(PhMe_2P)_2Re(N)Cl(S_2CNEt_2)$,[17] $(Et_2NCS_2)_3Mo(N)$ (**5**),[10] and $[Mo_2(S_2CNEt_2)_6](OTf)_2$ (**6**)[7] were prepared using literature procedures. All other reagents were commercially available and used without further purification.

NMR spectra were measured on a General Electric GN-300 or a Varian VXR-300 NMR spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra are reported in ppm referenced to tetramethylsilane; those for $^{31}P\{^1H\}$ NMR spectra are reported in ppm referenced to external 85% H_3PO_4. IR spectra were recorded as evaporated films on KBr plates on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Mass spectrometry (MS) spectra were obtained on a JEOL JMS-AX 505HA mass spectrometer using the fast atom bombardment (FAB) ionization mode and 3-nitrobenzyl alcohol as a matrix. In all cases, observed intensities were in satisfactory agreement with calculated isotopic distributions. Elemental analyses were performed by M−H−W Laboratories (Phoenix, AZ) or Canadian Microanalytical Services, Ltd. (Vancouver, British Columbia, Canada).

$[(PhMe_2P)_4ClRe(\mu\text{-}N_2)Mo(S_2CNEt_2)_3]OTf{\cdot}Et_2O$ ([7]OTf·Et₂O). In the drybox were placed **1** (108 mg, 0.13 mmol), **6** (90 mg, 0.065 mmol), and dry acetone (4 mL) in a 20-mL vial. The vial was securely capped, briefly agitated, and allowed to stand for 3 h. Dry ether (12 mL) was layered above the emerald-green solution. After 3 days, the crystals were collected by filtration in the drybox. Yield: 112 mg (55%). ^1H NMR (acetone-d_6): δ −3.83 (br, 24H, PCH_3), 1.87 (br, 18H, CH_2CH_3), 5.62 (br, 8H, ortho), 7.78 (br, 8H, meta), 8.43 (br, 4H, para), 23.29 (v br, 12H, CH_2CH_3). IR (cm^{-1}): 1818 (vs, $\nu_{N\equiv N}$), 1512 (vs), 1460 (m), 1436 (s), 1382 (w), 1358 (w), 1277 (s), 1224 (w), 1210 (w), 1151 (s), 1096 (w), 1076 (w), 1031 (m), 940 (m), 904 (s), 630 (m). Anal. Calcd for $C_{52}H_{82}N_5P_4S_7O_4F_3ClMoRe$: C, 39.87; H, 5.29; N, 4.47. Found: C, 39.80; H, 5.41; N, 4.53.

$[(PhMe_2P)_3(Et_2NCS_2)Re(\mu\text{-}N_2)Mo(S_2CNEt_2)_3]OTf$ ([8]OTf) was generated on a small scale by adding **2** (6.8 mg, 8.1 μmol), **6** (5.6 mg, 4.1 μmol), and dry acetone-d_6 (0.5 mL) to a valved NMR tube in the drybox. Over a 3-h period, the solution changed from brown to emerald green. ^1H NMR (acetone-d_6): δ −4.99 (s, 6H, PCH_3), −4.47 (s, 6H, PCH_3), −2.42 (s, 6H, PCH_3), −0.61 (s, 3H, CH_2CH_3 on Re), 0.76 (br, 3H, CH_2CH_3 on Re), 1.81 (br, 18H, CH_2CH_3), 6.27 (br, 4H), 6.70 (br, 2H), 7.56 (br, 2H), 8.15 (br, 1H), 8.32 (br, 4H), 8.79 (br, 2H), 17.69 (br, 2H, CH_2CH_3 on Re), 22.10 (v br, 12H, CH_2CH_3 on Mo), 34.59 (v br, 2H, CH_2CH_3 on Re). IR (cm^{-1}): 1829 (s, $\nu_{N\equiv N}$), 1510 (vs), 1460 (m), 1437 (s), 1382 (w), 1358 (m), 1276 (vs), 1224 (w), 1209 (m), 1151 (s), 1096 (w), 1076 (w), 1031 (m), 940 (m), 904 (s), 638 (m). FABMS: *m/z* 1318 ($M - H^+$).

$[(PhMe_2P)_4Re(N)Cl]OTf$ ([9]OTf). In the drybox were placed $(PhMe_2P)_3Re(N)Cl_2$ (606 mg, 0.884 mmol), AgOTf (Aldrich, 231 mg, 0.899 mmol), and dry $CHCl_3$ (10 mL) in a 20-mL vial. The vial was securely capped, briefly agitated, and allowed to stand for 10 min. The white solid was removed by filtration, and the yellow supernatant was transferred to a fresh 20-mL vial. This solution contains *mer*-$(PhMe_2P)_3Re(N)Cl(OTf)$,[18] which was characterized by $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −19.69 (t, $J = 14$ Hz, 1P), −7.31 (br, 2P). PMe_2Ph (Strem; 160 mg, 1.16 mmol) was added, and the vial was securely capped. After brief agitation, the vial was allowed to stand for 2 days. The solution was transferred to a

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50-mL round-bottomed flask, which was subsequently attached to a swivel frit. The apparatus was affixed to a vacuum line, and the volume of the solution was reduced to 2 mL. Ether (20 mL) was condensed above the yellow solution. The resulting pale-yellow solid was filtered and taken into the drybox. Yield: 608 mg (74%). ^{1}H NMR ($CDCl_3$): δ 1.83 (s, 24H, PCH_3), 7.37 (m, 12H, meta and para), 7.59 (br, 8H, ortho). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.9, 129.2, 131.1, 131.3, 134.4. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −24.85 (s, 4P). IR (cm^{-1}): 1774 (w), 1483 (m), 1436 (s), 1265 (vs, ν_{SO_3}), 1224 (s), 1151 (vs, ν_{CF_3}), 1100 (m), 1078 (w), 1051 (m), 1031 (vs, ν_{SO_3}), 1002 (m), 945 (s), 909 (vs), 845 (m), 746 (vs), 707 (s) 679 (m), 638 (s). FABMS: *m*/*z* 788 (M$^+$). Anal. Calcd for $C_{33}H_{44}NP_4ClO_3F_3SRe$: C, 42.29; H, 4.73; N, 1.49. Found: C, 42.50; H, 4.82; N, 1.63.

[(dcpe)$_2$Re(N)Cl]Cl ([10]Cl). This complex is mentioned in the literature,[19] but its synthesis, characterization, and spectroscopic properties are not discussed. The chloride salt was prepared by a method analogous to those reported for other bis(diphosphine) complexes.[15,20] In the drybox were placed $(Ph_3P)_2Re(N)Cl_2$ (640 mg, 0.804 mmol), dcpe (Strem; 700 mg, 1.66 mmol), and a magnetic stirbar in a 100-mL round-bottomed flask. A reflux condenser was attached to the flask, which was then affixed to the vacuum line. Dry C_6H_6 (40 mL) was added by vacuum transfer, and the solution was stirred at reflux under N_2 for 4 h. After the volume was reduced to 10 mL, hexane (40 mL) was layered above the dark-yellow solution. The next day, the yellow precipitate was collected on a glass frit in air, washed with hot hexane (20 mL) and ether (10 mL), and air-dried to yield 742 mg of [**10**]Cl (66%). ^{1}H NMR (CD_2Cl_2): δ 1.45 (m, 42H), 2.01 (m, 50H), 2.56 (br t, *J* = 11 Hz, 4H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.35 (pseudo quin, *J* = 10 Hz), 26.44 (s), 26.48 (s), 27.87 (two superimposed resonances), 28.10 (s), 28.31 (s), 28.80 (s), 29.92 (s), 30.06 (s), 30.19 (s), 34.94 (pseudo quin, *J* = 8 Hz), 37.99 (pseudo quin, *J* = 8 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −33.80 (s, 4P). IR (cm^{-1}): 2928 (vs), 2852 (vs), 1448 (s), 1418 (m), 1346 (w), 1270 (m), 1216 (w), 1173 (m), 1118 (m), 1075 (w), 1057 (m), 1003 (s, $\nu_{Re\equiv N}$), 916 (w), 890 (m), 851 (m), 810 (m), 730 (s), 697 (m), 661 (m). FABMS: *m*/*z* 1080 (M$^+$). Anal. Calcd for $C_{52}H_{96}Cl_2P_4Re$: C, 55.95; H, 8.67; N, 1.25. Found: C, 56.05; H, 8.44; N, 1.20.

***fac*-[(PhMe$_2$P)$_3$Re(N)(S$_2$CNEt$_2$)]OTf ([11]OTf)** was generated in solution on a small scale. In the drybox were added $(PhMe_2P)_2Re(N)Cl(S_2CNEt_2)$ (11.6 mg, 17 μmol), AgOTf (4.3 mg, 17 μmol), and CD_2Cl_2 (0.5 mL) to a 5-mL vial. The vial was securely capped, briefly agitated, and allowed to stand for 10 min. The yellow supernatant was syringed through a small piece of filter paper into an NMR tube. PMe_2Ph (Strem; 3.5 mg, 26 μmol) was added, and the tube was sealed with a Teflon-lined screw cap. The phosphine in [**11**]$^+$ trans to the nitride is in chemical exchange with free PMe_2Ph on the NMR time scale. ^{1}H NMR (CD_2Cl_2): δ 1.33 (t, *J* = 7 Hz, 6H, CH$_2$CH_3), 1.81 (d, *J* = 7 Hz, 6H, PCH_3 trans to nitride + free PhP(CH_3)$_2$), 1.81 (d, *J* = 10 Hz, 6H, PCH_3 cis to nitride), 1.93 (d, *J* = 10 Hz, 6H, PCH_3 cis to nitride), 3.65 (dq, *J* = 14 and 7 Hz, 2H, C*H*H′CH$_3$), 3.82 (dq, *J* = 14 and 7 Hz, 2H, CH*H′*CH$_3$), 7.44 (m, 9H, meta and para), 7.59 (m, 6H, ortho). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −22.15 (s, 2P, *P*Me$_2$Ph cis to N), −15.29 (br s, 1P, PMe$_2$Ph trans to N averaged with free PMe$_2$Ph).

***mer*-[Re(N)(PhMe$_2$P)$_3$Cl(μ-N)Mo(S$_2$CNEt$_2$)$_3$]OTf ([12]OTf)** was generated in solution by dissolving molybdenum nitride **5** and rhenium nitride [**9**]OTf in CD_2Cl_2. This reaction comes to equilibrium, and the starting materials, [**12**]$^+$ and PMe_2Ph, are observed by NMR. Alternatively, the complex can be generated by metathesis of $(PhMe_2P)_3Re(N)Cl_2$ with AgOTf in CD_2Cl_2 followed by the addition of **5**. ^{1}H NMR (CD_2Cl_2): δ 1.33 (m, 24H, dtc CH$_2$CH_3 + PCH_3), 1.98 (vt, J_{app} = 5 Hz, 6H, PCH_3), 2.24 (vt, J_{app} = 5 Hz, 6H, PCH_3), 3.79 (m, 12H, dtc CH_2CH$_3$), 7.04 (t, 1H, para), 7.20 (t, 2H, para), 7.36 (m, 10H, ortho, meta), 7.69 (d, 2H, ortho). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −10.06 (d, *J* = 17 Hz, 2P), −28.28 (t, *J* = 17 Hz, 1P). FABMS: *m*/*z* 1206 (M$^+$).

X-ray Structure Determination of [7]OTf·Et$_2$O. Green blocks of the salt were deposited after slow diffusion of ether into a solution of [**7**]OTf in acetone-d_6 (1:1, v/v) in the drybox. A 0.42 × 0.40 × 0.22 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 = 0.710 73 Å). The space group was identified as $P2_1/c$ based on systematic absences. The unit cell was determined based on 25 reflections with 15.0° < θ < 15.9°. The crystal quality was monitored by recording three standard reflections for approximately every 200 reflections measured; the decay was approximately 4%. An empirical absorption correction was applied (μ = 2.345 mm^{-1}; transmission factors 0.4336−0.5699). The Re and Mo atoms were located on a Patterson map. The remaining non-H atoms were found on difference Fourier syntheses. H atoms in the complex were placed in calculated positions. Final full-matrix least-squares refinement on F^2 converged at R1 = 0.0499 for 9867 unique reflections with $F_o > 4\sigma(F_o)$, R1 = 0.0654 for all 12 060 data (wR2 = 0.1213 and 0.1452, respectively). All calculations used *SHELXTL* (Bruker Analytical X-ray Systems), with scattering factors and anomalous dispersion terms taken from the literature.[21]

X-ray Structure Determination of [9]OTf. Yellow plates of the salt were deposited after slow diffusion of ether into a solution of [**9**]OTf in $CDCl_3$ (1:4, v/v). A 0.3 × 0.2 × 0.1 mm crystal was placed in an inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated using a Bruker SMART Apex system with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at −100 °C. The crystal was monoclinic and showed systematic absences due to a 2_1 screw axis. The *h*0*l* (*l* odd) reflections expected to be absent if a *c* glide were present were generally weak, but approximately one-third were observed [$I > 3\sigma(I)$]. Thus, the structure was solved and refined in the space group $P2_1$, with two independent molecules in the unit cell. The two molecules were related by an approximate inversion center, except for the occupancy of the disordered N≡Re−Cl unit (see below). The Re atoms were located on a Patterson map. The remaining non-H atoms were found by difference Fourier syntheses, and H atoms in the complex were placed in calculated positions. The nitride and chlorine were disordered in the two trans sites. Furthermore, refinement of the Re in the center of the molecule resulted in unrealistically high thermal parameters and a thermal ellipsoid elongated along the N−Cl axis, indicating that the Re atoms were disordered as well. Thus, each independent molecule was modeled with two sets of N≡Re−Cl groups, with site occupancies of the pseudo-inversion-related sets refining to 68.1(4)% in molecule 1 and 35.8(4)% in molecule 2. All non-H atoms except the nitride N were refined anisotropically. Final full-matrix least-squares refinement on F^2 converged at R1 = 0.0363 for 8954 reflections with $F_o > 4\sigma(F_o)$, R1 = 0.0445 for all 14 757 unique data (wR2 = 0.0815 and 0.0988, respectively).

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X-ray Structure Determination of [l0]$ReO_4 \cdot CH_2Cl_2 \cdot 1.5C_6H_6$. A solution of the chloride salt of [**10**]$^+$ was dissolved in dichloromethane and layered with benzene (1:4, v/v). This mixture was stored in a vial on the benchtop for 5 months, over which time decomposition supplied a small amount of ReO_4^-, allowing the nitride cation to crystallize as the perrhenate salt. A large pale-yellow block (0.94 × 0.30 × 0.21 mm) was coated in an inert oil and transferred to the tip of a glass fiber in the cold N_2 stream of a Bruker Apex CCD diffractometer ($T = -100$ °C). Data were reduced, correcting for absorption and decay, using the program *SADABS*. The crystal was triclinic (space group $P\bar{1}$). The Re, P, and Cl atoms were located using a Patterson synthesis, and remaining non-H atoms were found on difference Fourier syntheses. H atoms were placed in calculated positions. Final full-matrix least-squares refinement on F^2 converged at R1 = 0.0278 for 22 903 reflections with $F_o > 4\sigma(F_o)$ and R1 = 0.0345 for all 26 100 unique reflections (wR2 = 0.0694 and 0.0764, respectively).

X-ray Structure Determinations of Rhenium(I) Dinitrogen Complexes 2, 3·$2C_4D_8O$, and 4·$2CH_2Cl_2$. Orange plates of the dithiocarbamate complex **2** were deposited in a freezer overnight after slow diffusion of hexane into a solution of **2** in ether (1:1, v/v). A 0.20 × 0.17 × 0.09 mm crystal was examined on the Bruker SMART Apex system as described above for [**10**]ReO_4. Yellow plates of complex **3** were deposited after heating a solution of **3** in tetrahydrofuran-d_8 at 60 °C for 1 week under N_2. Yellow plates of the analogous bis(dicyclohexylphosphino)ethane complex were deposited after slow diffusion of ether into a solution of **4** in CH_2Cl_2/benzene (1:1, v/v). Suitable crystals of **3** and **4** were examined on an Enraf-Nonius CAD4 diffractometer as described above for [**7**]OTf. The Re centers in both **3** and **4** resided on crystallographic inversion centers, so the N_2 and Cl ligands were modeled as disordered about the inversion center with 50% occupancy in both sites. In **4**, anisotropic refinement of the two N atoms of the N_2 group failed, and they were refined isotropically. Further details are given in the Supporting Information.

Electrochemistry. Cyclic voltammetry was performed in the drybox using an EG&G Instruments PAR 283 potentiostat/galvanostat. A standard three-electrode setup was used. A Pt disk electrode was used as the working electrode (surface area ∼ 0.02 cm^2), a coiled Pt wire was used as the counter electrode, and a Ag wire was used as a pseudo reference electrode (−0.15 V vs SCE; measured in a 1.0 mM CH_3CN solution of $[Bu_4N]PF_6$). For [**7**]OTf·Et_2O, the test solution was prepared by adding the complex (12.9 mg, 8.6 μmol), $[Bu_4N]PF_6$ (0.39 g, 1.01 mmol, supporting electrolyte), and CH_3CN (8 mL) to the cell. A test solution of **1** was prepared analogously. In each case, the electrodes were connected to the potentiostat through electrical conduits in the drybox wall. Cyclic voltammograms were recorded with a scan rate of 100 mV s^{-1}.

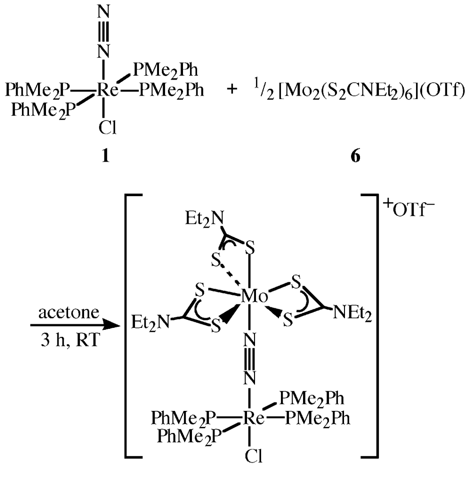
Reaction of 3 with 6. In the drybox were placed **3** (9.6 mg, 9.1 μmol), **6** (6.3 mg, 4.6 μmol), and CD_2Cl_2 (0.5 mL) in a valved NMR tube. The reaction progress was monitored over 24 h at 25 °C by observing the appearance of $[(dppe)_2ReCl_2]^+$.[22] ^{1}H NMR (CD_2Cl_2): δ 8.05 (d, $J = 6$ Hz, 16H, meta), 9.12 (t, $J = 8$ Hz, 8H, para), 9.60 (s, 8H, C*H*$_2$), 16.31 (d, $J = 8$ Hz, 16H, ortho).

Heating and Photolysis of [7]OTf. In the drybox were placed [**7**]OTf·Et_2O (20.0 mg, 13.4 μmol) and acetone-d_6 (0.5 mL) in each of two NMR tubes sealed to a ground-glass joint. Needle valves were attached, and the tubes were affixed to a vacuum line. The lower portions of the tubes were submerged in liquid N_2. After evacuation, the tubes were flame-sealed under vacuum and subsequently monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. One tube was immersed in a 60 °C oil bath, and the other was immersed in a beaker of water and irradiated in a Rayonet photochemical reactor equipped with 350-nm Ne bulbs.

Reaction of Rhenium(V) Nitrido Complexes with 5. In a typical experiment, in the drybox into an NMR tube sealed to a ground glass joint were added [**9**]OTf (14.3 mg, 16 μmol), PMe_2Ph (16 mg, 0.11 mmol), **5** (8 mg, 15 μmol), dimethyl terephthalate (internal standard), and CD_2Cl_2 (0.5 mL). A Teflon needle valve was attached, and the tube was affixed to a vacuum line. The lower portion of the tube was submerged in liquid N_2. After evacuation, the tube was flame-sealed under vacuum and subsequently monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, with heating by immersion in a 60 °C oil bath.

Results

Preparation and Characterization of μ-N_2 Complexes. Stirring the yellow rhenium(I) dinitrogen complex **1** with 0.5 equiv of the brown molybdenum(IV) complex **6** in acetone over 3 h yields an emerald-green solution of the N_2-bridged complex [**7**]OTf (eq 2). The addition of ether precipitates crystals of the air-sensitive salt [**7**]OTf·Et_2O in 55% yield. The complex is soluble in polar organic solvents such as CH_2Cl_2, CH_3CN, and tetrahydrofuran and insoluble in ether, benzene, and hexane.



(2)

As is typically seen upon coordination of Lewis acids to **1**, there is a reduction in the ν_{N_2} stretch in the IR (1818 vs 1925 cm^{-1} for **1**), with the stretch for [**7**]OTf in the low end of stretching frequencies observed for other bimetallic adducts of **1** (range 1795−1890 cm^{-1}).[8e] The paramagnetically shifted ^{1}H NMR spectrum shows six broad signals, with all of the dithiocarbamates and all of the phosphine ligands equivalent on the NMR time scale. Both the paramagnetism and fluxionality of the $Mo(S_2CNEt_2)_3$ fragment are typical of $(Et_2NCS_2)_3Mo^{IV}X$ complexes.[7] No ^{31}P NMR signals were observed for this paramagnetic species.

The structure of **7**$^+$ was determined by single-crystal X-ray diffraction (Tables 1 and 2). The solid-state structure (Figure 1) shows that the N_2 ligand of the Re^I complex binds to the $[Mo(S_2CNEt_2)_3]^+$ fragment derived from **6**. The Re atom remains in an octahedral environment, and the seven-

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Table 1. Crystallographic Data for [**7**]OTf·Et$_2$O, [**9**]OTf, and [**10**]ReO$_4$·CH$_2$Cl$_2$·1.5C$_6$H$_6$

	[**7**]OTf·Et$_2$O	[**9**]OTf	[**10**]ReO$_4$·CH$_2$Cl$_2$·1.5C$_6$H$_6$
empirical formula	$C_{52}H_{84}ClF_3MoN_5O_4P_4ReS_7$	$C_{33}H_{44}ClF_3NO_3P_4ReS$	$C_{62}H_{107}Cl_3NO_4P_4Re_2$
fw	1566.13	937.28	1533.12
T (K)	293	170	170
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
space group	$P2_1/c$	$P2_1$	$P\bar{1}$
total data collected	12 442	24 142	69 339
no. of indep reflns	12 060	14 757	26 100
a (Å)	18.729(2)	11.4696(5)	14.2776(4)
b (Å)	14.4370(13)	25.9841(12)	14.4176(5)
c (Å)	26.959(3)	12.8724(6)	17.1503(5)
α (deg)	90	90	73.543(1)
β (deg)	109.920(9)	91.587(1)	77.224(1)
γ (deg)	90	90	78.144(1)
V (Å^3)	6853.4(12)	3834.9(3)	3263.2(2)
Z	4	4	2
ρ_{calcd} (g cm^{-3})	1.518	1.623	1.560
cryst size (mm)	0.42 × 0.40 × 0.22	0.20 × 0.17 × 0.09	0.94 × 0.21 × 0.30
μ (mm^{-1})	2.345	3.508	3.972
R indices [$I > 2\sigma(I)$]^a	R1 = 0.0499, wR2 = 0.1213	R1 = 0.0363, wR2 = 0.0815	R1 = 0.0278, wR2 = 0.0694
R indices (all data)^a	R1 = 0.0654, wR2 = 0.1452	R1 = 0.0445, wR2 = 0.0988	R1 = 0.0345, wR2 = 0.0764

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [**7**]OTf·Et$_2$O

Re−N1	1.858(5)	Mo−S51	2.498(2)
Re−P1	2.448(2)	Mo−S52	2.518(2)
Re−P2	2.440(2)	Mo−S61	2.496(2)
Re−P3	2.466(2)	Mo−S62	2.490(2)
Re−P4	2.453(2)	Mo−S71	2.509(2)
Re−Cl	2.449(2)	Mo−S72	2.500(2)
Mo−N2	1.998(5)	N1−N2	1.167(6)
N1−Re−P1	87.05(15)	N2−Mo−S62	98.89(15)
N1−Re−P2	94.25(14)	N2−Mo−S71	88.92(15)
N1−Re−P3	90.09(15)	N2−Mo−S72	94.9(2)
N1−Re−P4	95.26(14)	S51−Mo−S52	68.29(6)
N1−Re−Cl	179.23(15)	S61−Mo−S62	70.66(6)
N2−Mo−S51	87.9(2)	S71−Mo−S72	68.57(6)
N2−Mo−S52	94.83(15)	N2−N1−Re	177.9(5)
N2−Mo−S61	169.51(15)	N2−N1−Mo	179.2(5)

coordinate Mo fragment retains its characteristic pentagonal-bipyramidal geometry. The N$_2$ bridge is essentially linear, with Re−N1−N2 and Mo−N2−N1 angles of 177.9(5)° and 179.2(5)°, respectively.

The N1−N2 distance in **7**$^+$ [1.167(6) Å] is similar to those seen in the previously reported heterobimetallic Re complexes (PhMe$_2$P)$_4$ClRe(μ-N$_2$)MoCl$_4$OMe [1.18(3) Å],[9b] [(PhMe$_2$P)$_4$ClRe(μ-N$_2$)]$_2$MoCl$_4$ [1.154(29) Å],[23] and [(PhMe$_2$P)$_4$ClRe(μ-N$_2$)Fe(OEP)]OTf [1.17(1) Å].[24] At first glance, this would appear to represent a substantial elongation of the N$_2$ ligand compared to the reported distance in **1** of 1.055(30) Å.[25] However, this value is chemically unreasonable, being noticeably shorter than the distance in free N$_2$ (1.0976 Å).[1b] The measured distance in **1** is probably distorted by the positional disorder of the N$_2$ ligand with the trans chloride; disorder may also explain the unreasonably short N−N distances reported for (PhEt$_2$P)$_4$ReH(N$_2$) [1.018(8) Å][26] and ([MeO]$_3$P)$_3$(MeNC)Re(Cl)(N$_2$) [1.038(21) Å].[27]

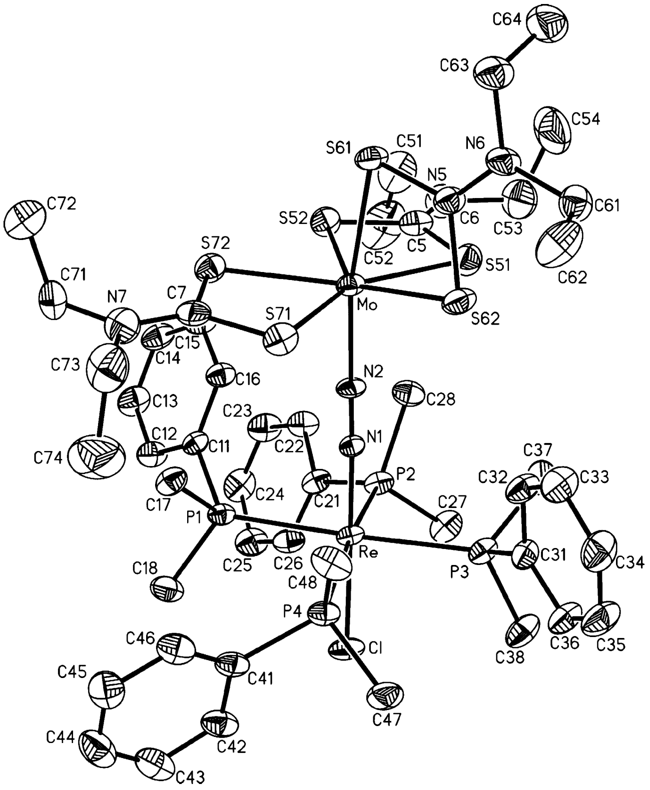

Figure 1. Thermal ellipsoid plot (30% ellipsoids) of the cation in [**7**]OTf·Et$_2$O. H atoms are omitted for clarity.

The only structurally characterized neutral, phosphine-rich rhenium(I) dinitrogen complexes with chemically reasonable N−N distances are (Me$_3$P)$_4$Re(NHPh)(N$_2$) [d_{NN} = 1.101(18) Å],[28] (PhMe$_2$P)$_3$(MeNC)Re(N$_2$)(S$_2$PPh$_2$) [d_{NN} = 1.126(13) Å],[29] and (dppe)$_2$Re(N$_2$)(NCS) [d_{NN} = 1.119(10)

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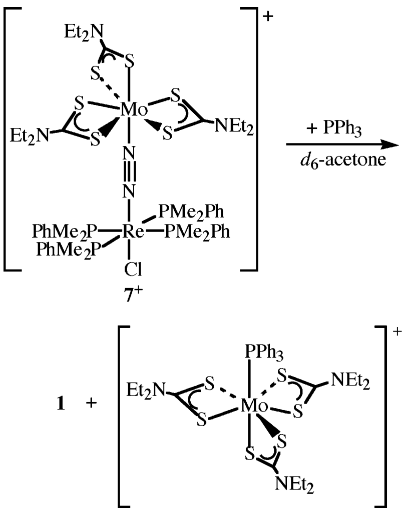
Å].[30] To clarify the true N−N distances in these mononuclear complexes, we determined the crystal structures of three previously prepared rhenium(I) dinitrogen complexes (Tables S1−S3 and Figures S1−S3 in the Supporting Information): **2**[12] [d_{NN} = 1.140(4) Å], **3**$\cdot$2C_4D_8O[13] [d_{NN} = 1.13(2)], and **4**$\cdot$2CH_2Cl_2[13] [d_{NN} = 1.139(13) Å]. The last two complexes do show Cl−N_2 disorder, but the fact that the groups are disordered about a crystallographic inversion center simplifies the disorder model and allows accurate determination of the N−N distance. In combination with the three literature structures with reasonable distances, one may conclude that the N−N distance in neutral, phosphine-ligated Re^I complexes is 1.126 ± 0.013 Å. Thus, complexing a second metal to the N_2 moiety, as in **7**$^+$, does result in a significant elongation of the N_2 ligand, but the effect is slight compared to highly activated μ-N_2 complexes such as $(R[Ar]N)_3Nb(\mu\text{-}N_2)Mo(NR[Ar])_3$ [d_{NN} = 1.235(10) Å].[3a]

The Re−N1 distance [1.858(5) Å] is slightly shorter than the corresponding distances in mononuclear N_2 complexes [for example, Re−N distances of 1.873(10) and 1.879(9) Å in **3** and **4**, respectively]. This is longer than the Re−N1 bond in $(PhMe_2P)_4ClRe(\mu\text{-}N_2)MoCl_4OMe$ [1.815(15) Å][9b] but is actually shorter than the formal Re−N double bond [1.901(5) Å] in the complex *trans*-$[Re(OH)(N{=}CMe_2)(dppe)_2][HSO_4]$.[31] The Mo−N2 distance [1.998(5) Å] is substantially shorter than a typical Mo−N dative bond (∼2.2−2.4 Å) but longer than the Mo−N bond in the diazenido complexes $Mo(N_2CO_2Et)(S_2CNMe_2)_3$ [1.732(5) Å][32] and $Mo(N_2Ph)(S_2CNMe_2)_3$ [1.781(4) Å].[33] This suggests that both the Re−N1 and Mo−N2 linkages have some multiple-bond character.

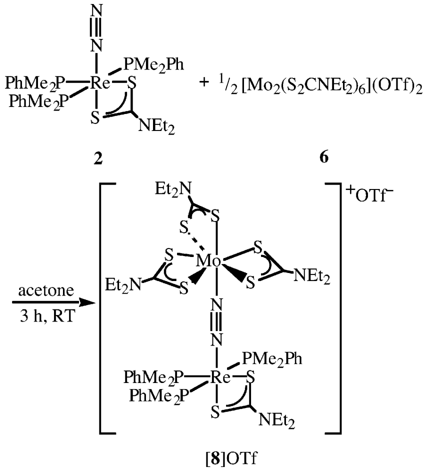
The N−N bonding and paramagnetism of **7**$^+$ can be rationalized using the classic four-atom model for bridging N_2 complexes.[34] In **7**$^+$, the out-of-phase metal π orbitals (back-bonding to the N_2 π* orbital) are filled and largely Re-centered, while the in-phase metal π orbitals (interacting weakly with the N_2 π-bonding orbital) are half-filled and largely Mo-centered. This picture is only slightly perturbed from the separated $L_4Re(X)(N_2)$ and $(Et_2NCS_2)_3MoX$ fragments, so that one could consider **7**$^+$ to be essentially a Lewis base adduct of **1** with the Lewis acid $(Et_2NCS_2)_3Mo^+$. Consistent with this formulation, when PPh_3 is added to [**7**]OTf in acetone-d_6, ligand substitution is observed over 2.5 h (eq 3). The known compound $[(Et_2NCS_2)_3Mo(PPh_3)]^+$ was identified by ^1H NMR spectroscopy as the product.[7]



7$^+$ **1** +

(3)

Several other rhenium(I) dinitrogen complexes react with **6** to form heterobimetallic N_2-bridged complexes analogous to **7**$^+$. The dithiocarbamate complex **2** reacts with **6** over 3 h in acetone-d_6 to produce an emerald-green solution of [**8**]OTf (eq 4). The IR spectrum of the emerald-green solution shows a strong ν_{N_2} stretch at 1829 cm^{-1}. The ^1H NMR spectrum for this complex, like that of [**7**]OTf, is also paramagnetically shifted but is considerably more complex because of its reduced symmetry. The observation of three phosphine methyl resonances of equal intensity indicates that the Re center has C_s symmetry. While this is consistent with either *fac* or *mer* geometry, in fact the *mer* geometry of the starting N_2 complex **2** appears to be retained, as judged by the presence of two signals for the rhenium dithiocarbamate methyl groups. (Only one set of methyl and methylene signals is seen for the fluxional $(Et_2NCS_2)_3Mo$ moiety.) The complex is stable for extended periods in solution under anaerobic conditions, but attempts to isolate [**8**]OTf led to decomposition. The complex **3** is only slightly soluble in acetone, but it decomposes in the presence of **6** into multiple species including the paramagnetic Re^{III} species *trans*-$[(dppe)_2ReCl_2]^+$.[22] Brief heating of **3** with **6** in dichloromethane yields an emerald-green solution, which is presumably the μ-N_2 complex $[(dppe)_2ClRe(\mu\text{-}N_2)Mo(S_2CNEt_2)_3]^+$. However, the green solution decomposes before conversion of **3** is complete, forming *trans*-$[(dppe)_2ReCl_2]^+$ and unidentified products. The complex **4** was not sufficiently soluble in polar organic solvents to explore its reactivity with **6**.



2 **6** [**8**]OTf

(4)

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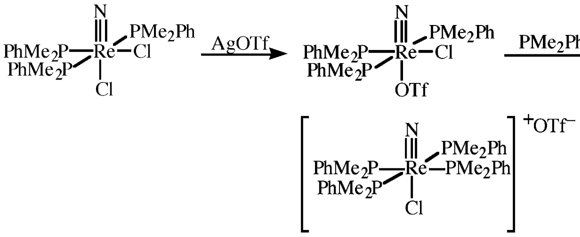
Preparation and Characterization of Nitrido Complexes. If the N_2-bridged complex $\mathbf{7}^+$ were to react by cleavage of the N−N bond, the products of the reaction would be the molybednum(VI) nitride **5** and the rhenium(V) nitride cation $\mathbf{9}^+$. The former complex is known,[10] but the latter is not. It was prepared by metathesis of $(PhMe_2P)_3Re(N)Cl_2$[14] with AgOTf to generate the pale-yellow complex *mer*-$(PhMe_2P)_3Re(N)Cl(OTf)$,[18] whose presence was confirmed by $^{31}P\{^1H\}$ NMR. The addition of PMe_2Ph to the triflate complex in situ yields cationic *trans*-[**9**]OTf, which is isolated as a pale-yellow air-stable salt (eq 5).



(5)

[**9**]OTf

The ^1H NMR spectrum shows a singlet (δ 1.83) for the methyl groups, consistent with C_{4v} symmetry. P−H coupling is absent, as in the N_2 complex **1** and other complexes with a square arrangement of phosphines.[35] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet in the upfield region (δ −24.85) typical for phosphine ligands in rhenium(V) nitrido complexes. The FABMS spectrum shows the parent ion $[\mathbf{9}]^+$ at *m*/*z* 788. Simple displacement of the triflate ligand by PMe_2Ph would place the phosphine in an axial position. It is well-precedented that harder ligands prefer to be trans to the nitride because this position has more ionic character.[36] Thus, an isomerization presumably occurs to form the observed product [**9**]OTf. Although many complexes of the form *trans*-$[Re(N)Cl(PP)_2]^+$ with chelating phosphines have been prepared,[15,19,20] complex $[\mathbf{9}]^+$ is the first example of a nitridorhenium(V) complex with four monodentate phosphines as equatorial ligands.

The square arrangement of the PMe_2Ph ligands in [**9**]OTf was confirmed by X-ray crystallography (Figure 2; for the minor component of molecule 1 and both components of molecule 2, see Figure S4 in the Supporting Information). Crystallographic details are listed in Table 1, and selected bond lengths and angles appear in Table 3. The Re−P bond distances (2.49 ± 0.02 Å on average) are slightly longer than those observed in $\mathbf{7}^+$ but are essentially identical to those found in the complex $[(dmppe)_2Re(N)Cl]^+$ [2.485(2) Å on average; dmppe = 1,2-bis[di(4-methoxyphenyl)phosphino]ethane].[20a] Disorder of the nitride and chloride prevents the determination of accurate bond distances for these ligands.[37]

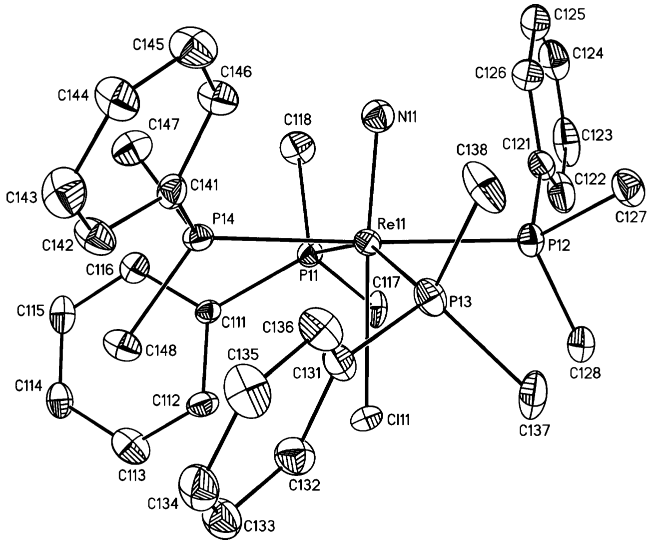


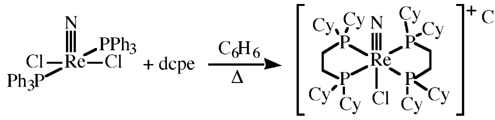
Figure 2. Thermal ellipsoid plot (30% ellipsoids) of one independent molecule of [**9**]OTf. Counterions and H atoms are omitted for clarity. The N≡Re−Cl unit is disordered; only the major component is shown.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Rhenium Nitride Complexes [**9**]OTf and $[\mathbf{10}]ReO_4{\cdot}CH_2Cl_2{\cdot}1.5C_6H_6$

	[**9**]OTf molecule 1[a]	[**9**]OTf molecule 2[a]	$[\mathbf{10}]ReO_4{\cdot}CH_2Cl_2{\cdot}1.5C_6H_6$
Re−N	1.773(14)[b]	1.807(11)[b]	1.677(2)
Re−Cl	2.523(4)	2.542(4)	2.5850(4)
Re−P1	2.496(3)	2.490(3)	2.4805(5)
Re−P2	2.505(3)	2.517(3)	2.5235(5)
Re−P3	2.509(3)	2.443(3)	2.5062(5)
Re−P4	2.466(3)	2.508(3)	2.5228(5)
N−Re−Cl	175.2(5)	176.1(4)	175.78(6)
N−Re−P1	100.8(4)	87.2(4)	92.94(6)
N−Re−P2	86.8(4)	95.5(4)	92.72(5)
N−Re−P3	99.8(4)	89.1(4)	100.01(6)
N−Re−P4	91.0(4)	102.6(4)	90.41(6)
P1−Re−P2	90.28(9)	90.45(10)	99.72(2)
P2−Re−P3	90.64(9)	91.38(10)	80.87(2)
P3−Re−P4	90.11(9)	90.55(10)	98.80(2)
P1−Re−P3	159.40(11)	175.96(12)	167.01(2)
P1−Re−P4	89.77(9)	88.83(10)	79.90(2)
P2−Re−P4	177.73(12)	161.83(12)	176.87(2)
Cl−Re−P1	78.68(10)	92.31(12)	89.49(2)
Cl−Re−P2	88.43(12)	80.62(12)	83.471(14)
Cl−Re−P3	80.77(11)	91.54(12)	77.65(2)
Cl−Re−P4	93.80(11)	81.28(12)	93.41(2)

[a] Metrical data are for the major component of the N≡Re−Cl disorder [68.1(4)% and 64.2(4)% for molecules 1 and 2, respectively]. Data for the minor components are in Table S4 in the Supporting Information. [b] N−Cl disorder renders these distances chemically unreliable; cf. ref 37.

The nitrido complex [**10**]Cl has been alluded to in the literature but without synthetic or spectroscopic details.[19] It was prepared using a procedure similar to those reported for other chelating bis(phosphine) complexes.[15,20] When the orange complex $(Ph_3P)_2Re(N)Cl_2$[16,38] is refluxed in benzene-containing dcpe, the triphenylphosphines and *cis*-chloride are replaced by 2 equiv of the bidentate phosphine to form the pale-yellow, air-stable solid [**10**]Cl (eq 6).



(6)

[**10**]Cl

Single crystals of the complex were grown over several months in a dichloromethane/benzene solution. The solid-

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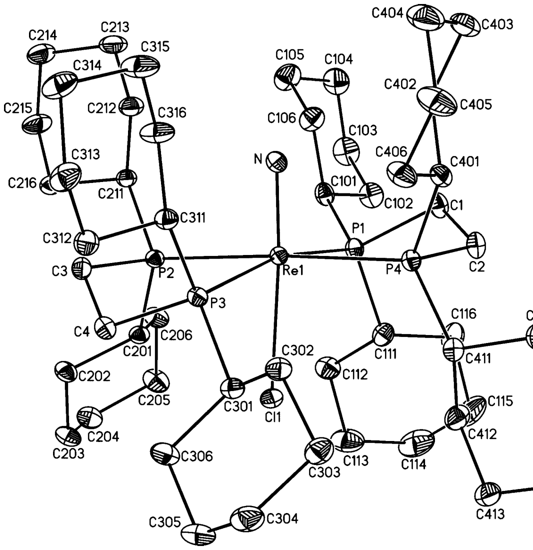
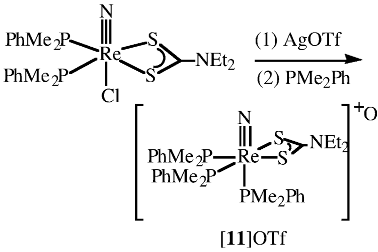


Figure 3. Thermal ellipsoid plot (40% ellipsoids) of the cation in [**10**]-$ReO_4 \cdot CH_2Cl_2 \cdot 1.5C_6H_6$. H atoms are omitted for clarity.

state structure (Figure 3) revealed the presence of ReO_4^- as the counterion, which undoubtedly formed from decomposition of [**10**]Cl over time. N−Cl positional disorder was not observed in the structure of [**10**]ReO_4, allowing the Re−N distance [1.677(2) Å] to be determined accurately. The Re−Cl distance [2.5850(4) Å] is substantially longer than that observed in, for example, $[\{HN(PPh_2)_2\}_2Re(N)Cl]^+$ [2.496(3) Å],[39] possibly because of the greater steric demand or electron donation by the trialkylphosphines. The Re−P distances [2.5103(5) Å on average] are longer than those in the related N_2 complex **4** [2.448(12) Å on average].

Mixed dithiocarbamato/dimethylphenylphosphine nitridorhenium(V) complexes have been studied by Abram[17,40,41] and others.[42] These complexes are all made from the precursor complex $(PhMe_2P)_3Re(N)Cl_2$ by metathesis; the extent of dithiocarbamate substitution into the Re coordination sphere is controlled by reaction stoichiometry. Surprisingly, a complex of the type $[P_3Re(N)(dtc)]^+$ was heretofore unknown. The complex [**11**]OTf is generated in solution by abstraction of chloride from $(PhMe_2P)_2Re(N)Cl(S_2CNEt_2)$[17] with AgOTf in CD_2Cl_2, followed by the addition of excess PMe_2Ph (eq 7). The $^{31}P\{^1H\}$ NMR spectrum shows two

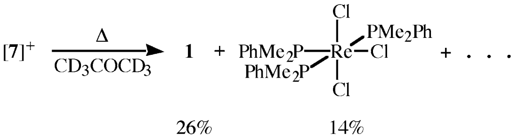


(7)

[**11**]OTf

singlets at δ −15.29 and −22.15. The absence of P−P coupling, as well as the absence of a signal for free PMe_2Ph (at δ −44) despite the presence of a slight excess of the phosphine, indicates that one of the bound phosphines is exchanging rapidly with free phosphine. In the ^1H NMR spectrum, diastereotopic methylene and equivalent methyl resonances are observed for the Et_2NCS_2 ligand, and the PCH_3 resonances appear as two doublets (J_{PH} = 10 Hz each) and a doublet with a coupling constant that is lower than expected (J_{PH} = 7 Hz); no virtual coupling is seen. These observations are consistent with a facial arrangement of the phosphines in which the phosphine trans to the nitride is in chemical exchange with free PMe_2Ph on the NMR time scale. It is unprecedented to observe soft phosphines binding trans to the nitrido ligand. In the related complex $(PhMe_2P)Re(N)(S_2CNEt_2)_2$, a dithiocarbamate ligand binds trans to the nitride in preference to PMe_2Ph.[17] The complex [**11**]OTf is stable in solution for over 3 days; no other isomers are observed.

Exploration of N_2 Cleavage and Nitrido Coupling. The μ-N_2 complexes [**7**]$^+$ and [**8**]$^+$ are stable in solution for 1 week at room temperature in the absence of O_2. Heating or photolysis of [**7**]OTf in acetone-d_6 did not result in N_2 cleavage; decomposition ensued, and **1**, *mer*-$ReCl_3(PMe_2Ph)_3$,[43] and other unidentified products were seen in the NMR (eq 8).



(8)

The electrochemistry of [**7**]OTf was examined by cyclic voltammetry in order to see if reductively induced N_2 cleavage was feasible. An irreversible reduction wave appears at $E_{p,c}$ = −0.20 V vs SCE. On the forward scan, two quasireversible oxidation waves are observed at 0.60 and 0.80 V vs SCE. Complex **1** (E_{ox} ~ 0.25 V vs SCE) is observed upon subsequent scans of [**7**]$^+$, which is consistent with studies done by Chatt,[11] which show that **1** and its bis(diphosphine) analogues undergo reversible one-electron oxidations. Reduction of [**7**]$^+$ with cobaltocene in tetrahydrofuran-d_8 results in the formation of **1** as identified by IR and ^1H and $^{31}P\{^1H\}$ NMR. Chemical reductions of the heterobimetallic tungsten μ-N_2 complexes $[(PhMe_2P)_4ClW(\mu\text{-}N_2)TiCpCl_2]$ and $[(PhMe_2P)_4ClW(\mu\text{-}N_2)NbCpCl_3]$ also result in recovery of the original anionic tungsten N_2 complex.[44]

The microscopic reverse of N_2 cleavage, nitrido coupling, was explored with **5** and the rhenium(V) nitrido complexes [**9**]OTf, [**10**]Cl, and the previously known nitride $[(dppe)_2Re(N)Cl]Cl$.[15,20] Equimolar amounts of [**9**]OTf and **5** react immediately in dichloromethane to give a deep-yellow solution. The aliphatic region of the ^1H NMR spectrum shows two virtual triplets and a doublet in a 1:1:1 ratio, consistent

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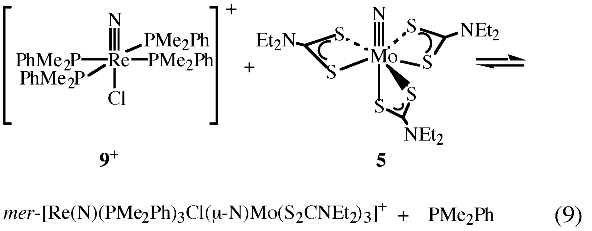
with the presence of three meridonal PMe_2Ph ligands in a complex possessing mirror symmetry. A new set of dithiocarbamato resonances is also observed, as well as free PMe_2Ph and unreacted **5** and **9**$^+$. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets (unreacted **9**$^+$ and free phosphine) and a mutually coupled doublet and triplet in a 2:1 ratio (J_{PP} = 17 Hz), which is also consistent with three meridonal phosphine ligands. Repeating the procedure with excess **5** drives the reaction to completion. The product thus appears to be the bimetallic μ-nitrido complex **12**$^+$ (eq 9), and its molecular formula was confirmed by observation of the parent ion at *m*/*z* 1208 in the FABMS spectrum. The ability of the nitride in **5** to bridge is well-precedented, with examples of bridges to Mo,[7,45] Os,[5] and main-group Lewis acids[46] being known. The NMR clearly establishes the *mer* stereochemistry of the phosphines in **12**$^+$, but whether the chloride is cis or trans to the terminal nitride could not be ascertained.



9$^+$ **5**

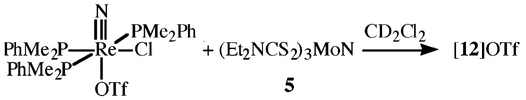
mer-$[Re(N)(PMe_2Ph)_3Cl(\mu\text{-}N)Mo(S_2CNEt_2)_3]^+$ + PMe_2Ph (9)

12$^+$

The reaction was repeated with varying concentrations of **9**$^+$, **5**, and PMe_2Ph and monitored by ^1H NMR to allow the equilibrium constant for eq 9 to be determined (eq 10). At

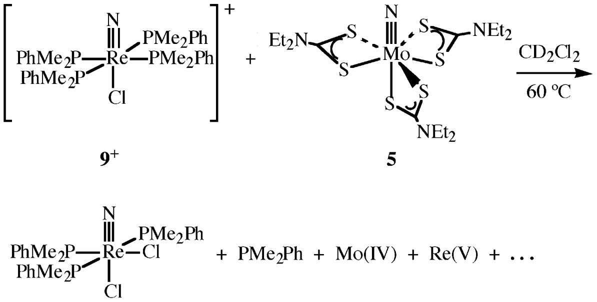
$$K_9 = \frac{[Re(N)(PMe_2Ph)_3Cl(\mu\text{-}N)Mo(S_2CNEt_2)_3{}^+][PMe_2Ph]}{[(PhMe_2P)_4Re(N)Cl^+][(Et_2NCS_2)_3MoN]} = 5.9 \pm 2.2 \quad (10)$$

25 °C, K_9 = 5.9 ± 2.2. The cationic complex **12**$^+$ can also be generated by treatment of $(PhMe_2P)_3Re(N)Cl(OTf)$ with **5** (eq 11). When an equilibrium mixture of **12**$^+$, **5**, and **9**$^+$,



5 (11)

generated by mixing **5** and [**9**]OTf, is heated in dichloromethane at 60 °C, **12**$^+$ is rapidly consumed and the parent nitrido complexes are depleted (<5% of each remaining after 10 h). ^1H and ^{31}P NMR spectra of the mixture show $(PhMe_2P)_3Re(N)Cl_2$, PMe_2Ph, and several unidentified diamagnetic and paramagnetic products (eq 12). Carrying out the reaction with excess PMe_2Ph, added to suppress the formation of **12**$^+$, gives similar decomposition rates and product distributions. Neither the N_2-bridged dimer **7**$^+$ nor the terminal N_2 complex **1** is observed in either case. Because **7**$^+$ decomposes into **1** under similar reaction conditions, if it had formed, it should have been easily identifiable. To verify that **1** would indeed be stable to these reaction conditions, the nitrides were reacted in the presence of added **1** and excess PMe_2Ph. The complex **1** did not react, and a similar product distribution was obtained. Dichloromethane solutions of [**10**]Cl and $[(dppe)_2Re(N)Cl]Cl$ do not react with **5** over 4 weeks at 60 °C.



9$^+$ **5**

(12)

Discussion

The cleavage of N_2 into terminal nitrides and its microscopic reverse, coupling of nitrides to form N_2, is a reaction of fundamental interest, as well as potential practical use, if the nitrides formed from N_2 can be converted into stable products while regenerating the metal complexes used for its reduction. Nitride coupling in Os complexes has been known for some time.[47] More recently, terminal ruthenium[48] and iron[49] nitrides have also been observed to couple to form N_2. Conversely, N_2 cleavage has been observed in complexes of Mo[2a−e] and Nb.[2f−h] Which metals undergo coupling, and which cleavage, is clearly due to periodic trends in the thermodynamics of the reaction, with electropositive early metals forming stronger bonds to N than the later transition metals.

To use N_2/nitride interconversions in catalysis, the reaction should optimally take place near thermoneutrality. Given the periodic trends mentioned above, this would indicate that the use of middle transition metals should be fruitful. Phosphine-ligated rhenium(V) nitrides, for example, are well-known but have not been reported to undergo coupling.[50] To increase the kinetic facility of the interconversion, we felt it would be useful to introduce polar effects into the reaction, which we had previously shown to increase the rate of nitride coupling.[5] Cummins has demonstrated that a mixed-metal Nb/Mo N_2 complex cleaves to nitrides much more rapidly than its isoelectronic Mo_2 analogue,[3a] though attribution of this to a purely kinetic effect is complicated by the presumably greater reducing power of the Nb

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(50) Diimine-ligated rhenium(V) nitrides have been reported to undergo reduction under forcing conditions (200 °C), possibly by elimination of N_2. Jabs, W.; Herzog, S. *Z. Chem.* **1972**, *12*, 297.

analogue. To implement this approach, it was necessary to approach eq 1 from both directions by exploring the reactivity of a heterobimetallic dimeric M—N≡N—**M** and the related isomeric nitrides M≡N and **M**≡N. Cases where μ-N_2 complexes are known to be isomeric with stable nitrides are extremely rare. They include Cummins' (μ-N_2){Mo(N[R]-Ar)$_3$}$_2$/(N)Mo(N[R]Ar)$_3$ system (where N_2 cleavage is observed)[2a,b] and Schrock's (μ-N_2){Mo[N_3N]}$_2$/(N)Mo[N_3N] system (which are not reported to interconvert).[51,52]

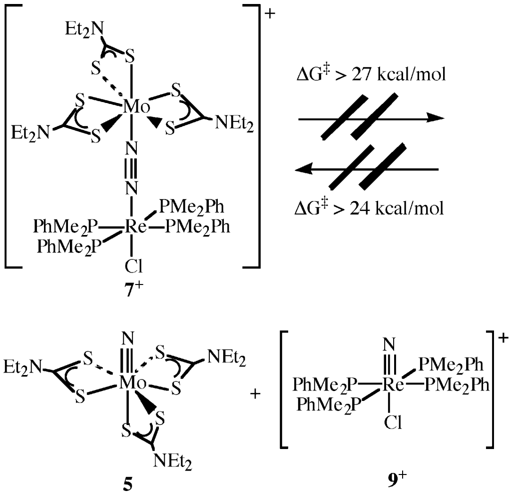
Phosphine-rich rhenium(I) dinitrogen complexes (e.g., **1**−**4**) were ideal candidates for the four-electron redox partner ("N^+" acceptor). Not only does Re have a stable and easily accessible +5 oxidation state, but the rhenium(V) nitrido analogues of **1**−**4** were either already known ([(dppe)$_2$Re(N)Cl]$^+$) or seemed trivial to prepare ([**10**]$^+$). Indeed, the cationic nitrido complexes [**9**]$^+$, [**10**]$^+$, and [**11**]$^+$ were readily prepared and proven to be stable and unexceptional in their properties. Thus, it seemed possible that the Re^I partner could provide four of the six electrons required for N_2 cleavage.

Finding an "N^-" acceptor was more problematic, requiring a complex with a vacant or loosely filled coordination site, as well as the ability to undergo a two-electron oxidation to a nitride. We had previously found that the dimeric complex **6** serves as a source of the [Mo(S_2CNEt_2)$_3$]$^+$ fragment when treated with a variety of ligands. In particular, it can serve as an "N^-" acceptor, reacting with NaN_3 to form **5** via the intermediate azido complex.[7]

Chatt[8] and others[9] had shown previously that N_2 complex **1** reacts with Lewis acids to form μ-N_2 complexes. It reacts similarly with **6** to form the heterobimetallic adduct [**7**]OTf, which was isolated. This adduct was crucial to the study of the N_2 cleavage/nitrido coupling from both directions, which was now possible because the isomeric nitrido complexes were in hand.

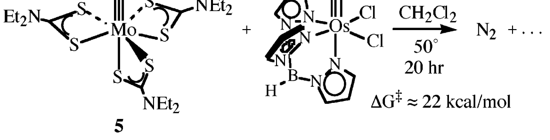
The spectroscopic and structural features of [**7**]OTf indicated that cleavage of the N_2 ligand might be attainable in this complex. The IR spectrum indicated moderate weakening of the N−N bond (1818 vs 1925 cm^{-1} for **1**), and the paramagnetic ^{1}H NMR spectrum suggested that some electron transfer had occurred. The X-ray crystal structure showed modest lengthening of the N−N bond [1.167(6) Å] and noticeable Re−N1 and Mo−N2 multiple bonding. However, chemical reduction, heating, or photolysis of [**7**]$^+$ leads only to decomposition of the dimer into the terminal N_2 complex **1** (and several unidentified products in the latter two cases). Thus, it appears that N_2 cleavage is precluded by one or more decomposition pathways.

Mixing **5** and [**9**]$^+$, the isomeric nitrides of [**7**]$^+$, instantly induces [**9**]$^+$ to bind **5** to form an equilibrium mixture containing the μ-nitrido adduct ([Re(N)(PhMe$_2$P)$_3$Cl(μ-N)-Mo(S_2CNEt_2)$_3$]$^+$ ([**12**]$^+$) and free PMe$_2$Ph (eq 9). Heating the equilibrium mixture leads to decomposition, whose rate is unaffected by excess PMe$_2$Ph (which does suppress μ-nitrido formation). This establishes that the reverse process, nitrido coupling, is also precluded by a decomposition pathway. This inability to interconvert between [**7**]$^+$ and its isomeric nitrides **5** and [**9**]$^+$ establishes that there are *kinetic* factors that preclude N_2 cleavage and nitrido coupling in this system. The activation barrier for N_2 cleavage and nitrido coupling must be higher than the barriers for the decomposition reactions (eq 13). Of course, it is possible that an analogous, but more thermally robust, system might be coaxed into undergoing N_2 cleavage or nitride coupling at higher temperatures than are achievable in this system. The present results suggest that such a reaction, even if achievable, would take place with a sizable energetic barrier. The great thermodynamic stability of N_2 is often adduced as the major problem in coaxing reactivity out of this notoriously inert molecule. This example emphasizes that this cannot be the whole explanation for N_2's stability, for here neither its breakup *nor its formation* is kinetically accessible.



(13)

Both nitrides in eq 13 are nucleophilic, as judged by the known chemistry of **5**[53] and of rhenium(V) nitrido complexes. In retrospect, therefore, it is perhaps not surprising that nitride coupling (or N_2 cleavage) should be kinetically difficult in this system because nucleophiles do not react readily with other nucleophiles. A key question is whether modifications to the M(μ-N_2)**M**/M≡N,**M**≡N system can improve the kinetic factors involved in N_2 cleavage/nitride coupling. Specifically, if one could make a nucleophilic and electrophilic nitride from N_2, one would expect enhanced kinetic facility for the reaction. This has been demonstrated in the direction of nitride coupling, in the reactions of electrophilic osmium(VI) nitrides: TpOs(N)Cl$_2$ [Tp = hydridotris(1-pyrazolyl)borate] reacts readily with **5** to form N_2 (eq 14).[5]



(14)

There is, however, a problem in applying this strategy to N_2 cleavage. Osmium(VI) nitrides are electrophilic because

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(52) With the preparation of [**9**]OTf reported here, the unsymmetrical μ-N_2 complex [(PhMe$_2$P)$_4$ClRe(μ-N_2)Cr(OEP)][OTf][24] is a further example because (OEP)Cr(N) is known: Buchler, J. W.; Dreher, C.; Lay, K.-L.; Raap, A.; Gersonde, K. *Inorg. Chem.* **1983**, *22*, 879−884.

of the high electronegativity of the metal center, which lowers the energy of the M≡N π^* orbital and gives that orbital substantial N character.[54] The same factors that make the nitride more electrophilic also make it more oxidizing, with the net result that Os^{VI}/Mo^{VI} thermodynamically favors nitride coupling, not N_2 cleavage. This analysis thus leads to the unfortunate conclusion that the factors that might accelerate cleavage kinetically (introducing a polar effect through an electrophilic nitride) will also tend to render it thermodynamically inaccessible (by making the nitride more oxidizing). Strategies other than changing the metal center to increase the electrophilicity in one of the product nitrides, such as changes in ancillary ligands, might partially circumvent this correlation, but the general association between the Lewis acidity and oxidizing power suggests that such manipulations will also be tricky to achieve. This tension between increasing polarization and decreasing reducing power is thus a significant stumbling block in implementing the otherwise plausible strategy of using polar effects to promote N_2 cleavage at low driving force.

Conclusions

The previously known rhenium(I) dinitrogen complexes **1** and **2** react with the "N^-" acceptor **6** to form the N_2-bridged adducts $\mathbf{7}^+$ and $\mathbf{8}^+$. Structural and spectroscopic data show that the N≡N bond is slightly weakened, but cleavage is not observed. The stability of $\mathbf{7}^+$ cannot be due solely to thermodynamic factors because the isomeric nitrides $\mathbf{9}^+$ and **5** do not react with each other. Because the same factors that would likely promote N_2 cleavage kinetically, such as polarization of the nitrides into a nucleophilic and an electrophilic component, also thermodynamically favor nitride coupling over N_2 cleavage, it appears that N_2 cleavage to terminal nitrides at low driving forces will be difficult to accelerate through the use of polar effects.

Acknowledgment. We thank Dr. Maoyu Shang for his assistance with the X-ray structures of $\mathbf{3}\cdot 2C_4D_8O$, $\mathbf{4}\cdot 2CH_2Cl_2$, and $\mathbf{7}[OTf]\cdot Et_2O$ and Dr. Alicia Beatty for her help with the X-ray structures of **2**, [**9**]OTf, and $[\mathbf{10}]ReO_4\cdot CH_2Cl_2\cdot 1.5C_6H_6$. Support from the National Science Foundation (Grant CHE-97-33321-CAREER), the Camille and Henry Dreyfus Foundation (New Professor Award), DuPont (Young Professor Award), the Dow Chemical Co. (Innovation Recognition Program), and the Arthur J. Schmitt Foundation (fellowship to S.B.S.) is gratefully acknowledged.

Supporting Information Available: Tables of crystallographic parameters, selected bond lengths and angles, and thermal ellipsoid plots for **2**, $\mathbf{3}\cdot 2C_4D_8O$, and $\mathbf{4}\cdot 2CH_2Cl_2$, and thermal ellipsoid plots and selected bond lengths and angles for all components of disordered [**9**]OTf and crystallographic information for all structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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