1622 *Organometallics* **2000,** *19,* 1622−1624

Dinitrogen Cleavage Stemming from a Heterodinuclear Niobium/Molybdenum N$_2$ Complex: New Nitridoniobium Systems Including a Niobazene Cyclic Trimer

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Received February 17, 2000

Summary: Preparation of the terminal nitrido anion $^-$*[NNb(N[*^{i}*Pr]Ar)*$_3$*] and the niobazene trimer {(*μ*-N)Nb(N[*^{i}*Pr]Ar)*$_2$*}*$_3$ *(*^{i}*Pr = CH(CH*$_3$*)*$_2$ *or CH(CD*$_3$*)*$_2$*, Ar = 3,5-C*$_6$*H*$_3$*Me*$_2$*) entails cooperative splitting of dinitrogen upon reduction of the heterobimetallic paramagnetic dinitrogen complex (Ar[R]N)*$_3$*Mo(*μ*-N*$_2$*)Nb(N[*^{i}*Pr]Ar)*$_3$ *(R =* ^{t}*Bu or C(CD*$_3$*)*$_2$ *CH*$_3$*).*

Dinitrogen gas rarely is employed as the nitrogen source in the synthesis of molecular nitridometal compounds,[1] but recent advances involving well-defined N$_2$-splitting reactions are improving the outlook for the direct utilization of molecular nitrogen. Dimolybdenum systems[2−4] have been found to effect N$_2$ splitting in the absence of added reagents, while certain diniobium and divanadium systems[5−7] also split dinitrogen when used in conjunction with alkali metals. While dinuclear dinitrogen complexes represent an emerging theme for N$_2$-splitting systems,[2−6,8−12] thus far the systems in question have been homobimetallic in nature. The present work shows that molybdenum and niobium can be used together to effect the splitting of molecular nitrogen in a cooperative fashion. Nitridoniobium compounds stemming from this intriguing heterodinuclear N$_2$-scission process include a niobazene cyclic trimer, the structure of which provides insight into the bonding in M$_3$N$_3$ rings (M = transition metal).[13−15]

Recent work with anionic molybdenum dinitrogen complexes has shown them to be good nucleophiles, in that they are smoothly alkylated or silylated at the β (terminal) nitrogen atom.[16−18] For example the anion [(N$_2$)Mo(N[R]Ar)$_3$]$^-$ is converted to Me$_3$SiNNMo(N[R]Ar)$_3$ and MeNNMo(N[R]Ar)$_3$ upon reaction with chlorotrimethylsilane and methyl tosylate, respectively. Furthermore, it has been possible to assemble a variety of heterodinuclear dinitrogen complexes by reaction of dinitrogen molybdenum complex anions with various metal halide (M = Zr, V, Fe, and U) electrophiles.[16,17,19,20] Accordingly, we find that the reaction of the purple chloroniobium(IV) complex NbCl(N[^{i}Pr]Ar)$_3$[21] with [Na(THF)$_x$][(N$_2$)Mo(N[R]Ar)$_3$][18] or [Mg(THF)$_2$][(N$_2$)Mo(N[R]Ar)$_3$]$_2$[21] provides in high yield (74−78%) the neutral, paramagnetic, brown-green N$_2$-bridged complex (Ar[^{t}Bu]N)$_3$Mo(μ-N$_2$)Nb(N[^{i}Pr]Ar)$_3$ (**2**,[21] Figure 2).

Complex **2** is characterized by an intense ν_{NN} at 1583 cm^{-1}, a value to be compared with that (1548 cm^{-1}) for the isotopomer prepared from ^{15}N$_2$. While EPR spectroscopy (25 °C, toluene) revealed a classic 10-line pattern resulting from coupling to the $I = 9/2$ niobium nucleus ^{93}Nb (100%), no coupling to the spin 5/2 molybdenum nuclei ^{95}Mo and ^{97}Mo (15.92% and 9.55%, respectively) was resolved.[21] The magnitude of the ^{93}Nb coupling was found by simulation to be 99.3 G, a value typical for niobium(IV) systems of the type Nb(X)(N[^{i}Pr]Ar)$_3$ (X$^-$ = I, Cl).[22] Inclusion in the simulation of a 32.0 G coupling to $^{95/97}$Mo (this value being typical for $S = 1/2$ molybdenum systems of the type MoCl$_2$(N[^{i}Pr]Ar)$_3$)[23] did not lead to resolution of the molybdenum hyperfine. Thus one cannot conclude that

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10.1021/om000159k CCC: $19.00

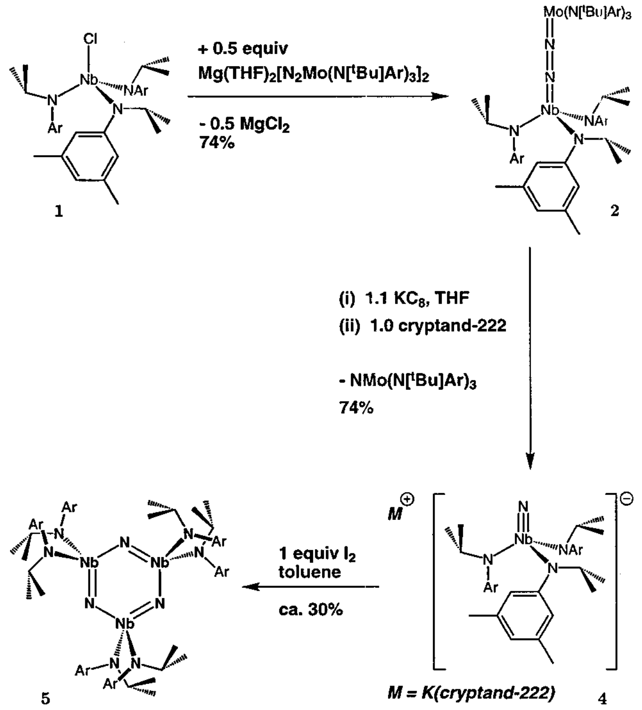

Figure 1. Preparation of niobazene trimer **5**. Monochloride **1** was obtained by reduction of the corresponding niobium(V) dichloride $NbCl_2(N[^iPr]Ar)_3$ (see Supporting Information.

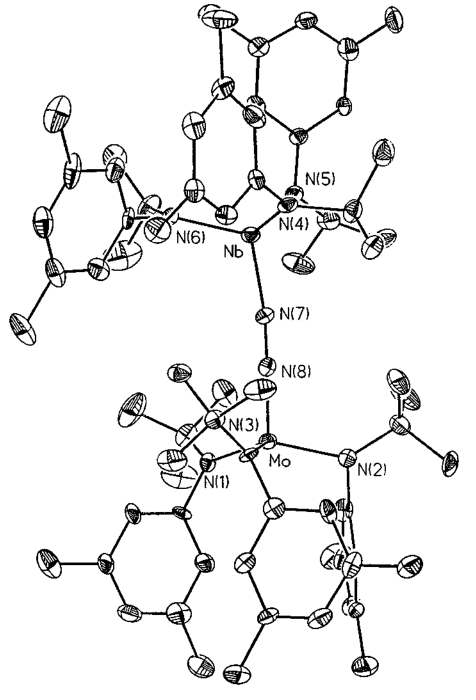

Figure 2. Structural diagram of $(Ar[^tBu]N)_3Mo(\mu\text{-}N_2)Nb(N[^iPr]Ar)_3$ (**2**) with ellipsoids at the 35% probability level. Selected distances (Å) and angles (deg): Nb−N(7), 1.969(9); Nb−N(6), 1.991(8); Nb−N(5), 1985(8); Nb−N(4), 2054(8); Mo−N(8), 1.783(9); Mo−N(1), 2.009(8); Mo−N(2), 1.971(8); Mo−N(3), 1.974(8); N(8)−N(7), 1.235(10); Mo−N(8)−N(7), 1.78(10); N(8)−N(7)−Nb, 167.0(8).

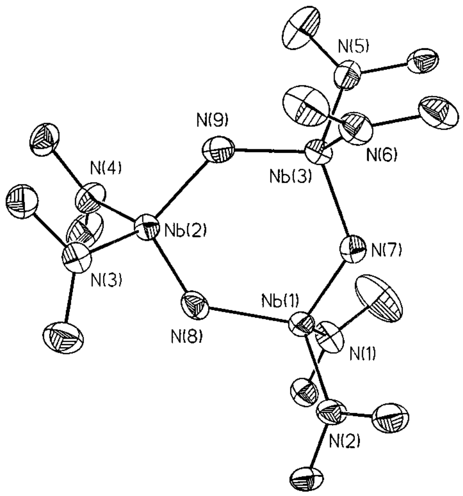

Figure 3. Structural diagram of $\{(\mu\text{-}N)Nb(N[^iPr]Ar)_2\}_3$ (**5**) with ellipsoids at the 35% probability level. Selected distances (Å) and angles (deg): Nb(1)−N(7), 1.792(6); Nb(1)−N(8), 2.004(6); Nb(2)−N(8), 1.795(7); Nb(2)−N(9), 2.003(6); Nb(3)−N(9), 1.785(6); Nb(3)−N(7), 2.004(6); Nb(1)−N(7)−Nb(3), 129.4(3); N(8)−Nb(1)−N(7), 110.6(3); N(7)−Nb(3)−N(9), 110.2(3); Nb(3)−N(9)−Nb(2), 130.2(3); N(9)−Nb(2)−N(8), 110.0(3). Peripheral substituents are omitted for clarity.

the odd electron in $S = 1/2$ **2** ($\mu_{eff} = 2.3\ \mu_B$) is localized exclusively on niobium. Indeed, density funtional theory (DFT) calculations[24−26] indicate that the orbital housing the odd electron possesses both Mo (22%) and Nb (29%) character. The calculations also indicate that the color of complex **2** is due to a $\pi \rightarrow \sigma^*$ transition, where the σ^* orbital in question is localized primarily on Mo and oriented largely distal to the bridging N_2 ligand.[24−28]

Structural characterization of complex **2** was achieved by single-crystal X-ray diffraction (Figure 2). The topologically linear Nb−N−N−Mo core exhibits respective distances of 1.969(9), 1.235(10), and 1.783(9) Å, highlighting the asymmetry in the bonding of N_2 to the two metals. In addition, the solid-state structure of complex **2** reveals distortion with a descent in symmetry from an ideal C_3 to the observed C_1 resulting from an amide rotation and bending about the $Nb-N_2-Mo$ frame. Electrochemically it was found that **2** undergoes a reversible oxidation at −1.4 V (vs Fc/Fc^+), in accord with which chemical oxidation provided the cation $[(Ar[^tBu]N)_3Mo(\mu\text{-}N_2)Nb(N[^iPr]Ar)_3]^+$, as its scarlet-colored $[B(3,5\text{-}C_6H_3(CF_3)_2)_4]^-$ salt, in 77% isolated yield. When prepared using $^{15}N_2$, the latter cation exhibited two ^{15}N NMR signals, located at 429.8 and 415.9 ppm and mutually related by a coupling of 15 Hz. Possibly due to coupling to ^{93}Nb, the 415.9 ppm signal was severely broadened at 25 °C but relatively sharp at −40 °C.[29]

The electrochemistry[21] of **2** revealed an irreversible reduction at ca. −2.6 V, successive scans resulting in the production of a new quasi-reversible wave at −2.8 V, a value characteristic of the terminal molybdenum(VI) nitrido derivative $N{\equiv}Mo(N[R]Ar)_3$.[18] This reduction was investigated *chemically* by reaction of complex **2** with KC_8 [30] in THF solution. As indicated in

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Figure 1, treatment of **2** with KC_8 followed by the addition of the cryptand 2,2,2-Kryptofix resulted in the isolation in 74% yield of the diamagnetic $[K(2,2,2\text{-Kryptofix})]^+$ salt of the nitrido anion $[NNb(N[^iPr]Ar)_3]^-$ (**4**), which was separated easily from the neutral Mo nitride $N{\equiv}Mo(N[R]Ar)_3$. Colorless nitridoniobium anion $[NNb(N[^iPr]Ar)_3]^-$ exhibited proton NMR spectra characteristic of a single-$N(^iPr)Ar$ ligand environment, and when prepared from $^{15}N_2$, evinced a singlet at $\delta = 793$ ppm in its ^{15}N NMR spectrum. The latter large downfield shift is typical of terminal, d^0 nitrido derivatives.[2,31-35] Salt **4** also was characterized by single-crystal X-ray diffraction methods,[36] confirming that the compound consists of discrete anions and cations and that the terminal nitrido functionality ($d_{Nb-N} = 1.696(5)$ Å) was obtained as a mononuclear, pseudo-3-fold symmetric anion.

Treatment of nitrido anion **4** with iodine (1.0 equiv) gave a mixture of products from which the niobazene cyclic trimer $\{(\mu\text{-}N)Nb(N[^iPr]Ar)_2\}_3$ (**5**) was obtained in 27% yield after purification by recrystallization. This result was unexpected in that the related nitridoniobium anion $^-[NNb(N[R]Ar)_3]$[37] is known to react smoothly with iodine (1.0 equiv) to give the neutral iodoimido complex $INNb(N[R]Ar)_3$.[38] Treatment of **4** with $[FeCp_2]^+$ (triflate salt) also was found to produce appreciable quantites of trimer **5** in better yields (41%). Diamagnetic **5** exhibits ^1H and ^{13}C NMR spectra in accord with its crystallographically determined (Figure 3) pseudo-C_{3h}-symmetric molecular structure, and the ^{15}N NMR signal for the isotopically labeled trimer consists of a singlet located at $\delta = 592$ ppm.

Bond length alternation around the Nb_3N_3 ring is a salient crystallographic finding for trimer **5** (Figure 3), the average "short" Nb=N bond being 1.791(7) Å, while the "long" bond to the bridging nitrido ligands averages to 2.004(6) Å. Such bond length alternation contrasts sharply with results reported previously for related "triazatrimetallabenzenes" of formula $\{(\mu\text{-}N)TaCp^*(X)\}_3$, where X = Cl or Me.[13,14] Structures of the latter two compounds revealed equivalent Ta−N bonds in the respective Ta_3N_3 rings, a result interpretable either in terms of the disparity in electronegativity between Ta and N or alternatively in terms of delocalized bonding. Careful inspection of the structure of trimer **5** suggests a different explanation, an explanation based on the π-donor properties of the planar amido ligand vis-à-vis the *cylindrical* nature of Cp* and chloride ligands in the tantalum compounds. Focusing attention on Nb(1) in Figure 3, the relevant structural parameter is the C(17)−N(1)−Nb(1)−N(7) dihedral angle of near 0° (1.09(1.11)°). This dihedral angle positions the lone-pair p orbital on N(1) exactly orthogonal to the *short* nitrido Nb(1)−N(7) bond. Structure optimizations using DFT calculations on the model system[39,40] $\{(\mu\text{-}N)Nb(NH_2)_2\}_3$ showed the rotation about the metal amido bonds to correlate directly with the μ-nitride bond lengths around the Nb_3N_3 ring.[21] The six Nb−μ−N distances become equivalent when the amide rotation angle permits an increase in symmetry to D_{3h}, but such a structure is energetically less favorable. The observed structure in C_{3h} can be thought of as enjoying second-order Jahn−Teller stabilization,[41] not attainable in the previously reported tantalum systems due to the cylindrical nature of the π-donor ancillary ligands employed.

Acknowledgment. For financial support are gratefully acknowledged the National Science Foundation (CAREER Award CHE-9501992), the Alfred P. Sloan Foundation, the National Science Board (1998 Alan T. Waterman award to C.C.C.), and the Packard Foundation. K.M. thanks the Deutsche Forschungsgemeinschaft for financial support. The authors would like to thank Prof. Luis Baraldo for cyclic voltammetry measurements and Dr. Jeffrey H. Simpson and Dr. Mark Wall for ^{15}N NMR experiments.

Supporting Information Available: Synthetic, spectroscopic, and analytical details for new complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000159K

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