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Stepwise Reduction of Dinitrogen to Nitride Assisted by Niobium Bonded to Oxygen Donor Atoms: The Potential of Reduced Forms of Niobium Calix[4]arene

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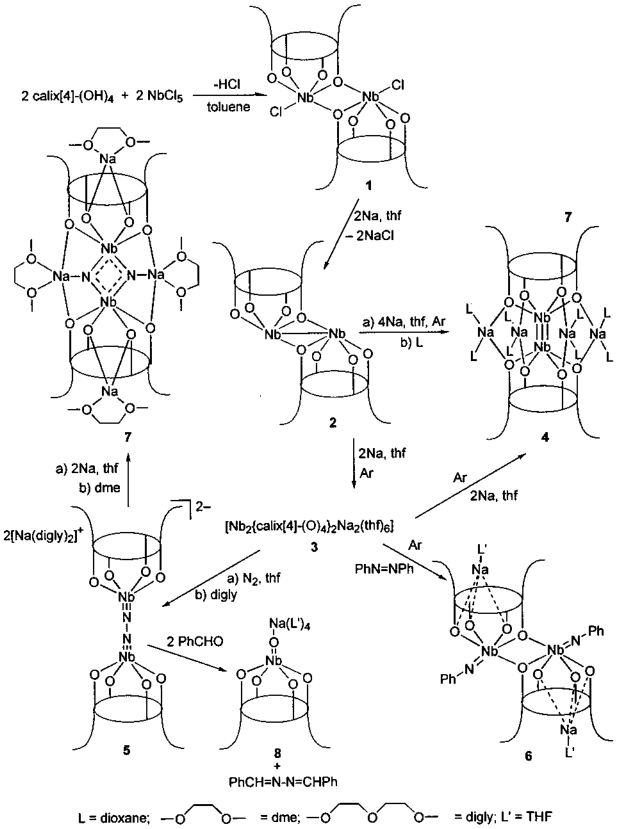
Our approach for mimicking the reduction of nitrogen with transition metal complexes,[12] in an oxygen-rich environment[3] centers on the utilization of low-valent niobium[4] bound to the calix[4]arene tetraanion.[5] Such species can react to form metal−metal-bonded dimers or to reduce and cleave, under appropriate conditions, N−N multiple bonds.

Scheme 1 displays the relationship between these two reaction pathways. The stepwise reduction of **1** under argon using Na metal in THF allowed for the isolation and identification of **2**,[6] **3**,[7] and **4**.[8] The use of an Ar atmosphere is necessary for obtaining **3** and **4**, since the reduction of **2** under N_2 led to a mixture of unidentified products. Complexes **2** and **4** have been structurally characterized [Nb−Nb, 2.757(1) Å, **2**; 2.385(2) Å, **4**],[9] while the X-ray structure of **3**, the key compound in this context, is not yet available. In the solid state it is essentially diamagnetic,[10] but this does not allow us to easily indicate by which mechanism, antiferromagnetic interaction or a double metal−metal bond, the two Nb ions couple. Complex **3** reacts with N_2 to form **5**.[11]

Scheme 1



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(6) Procedure for **2**: Sodium (0.52 g, 22.5 mmol) and naphthalene (0.904 g, 7.06 mmol) were added to a THF (380 mL) suspension of **1**$(C_7H_8)_{2.6}$ (19.90 g, 11.14 mmol), and the reaction was stirred at room temperature for 3 days. The solid residue was extracted with the mother liquor for 40 h, volatiles were removed in vacuo, and the brown microcrystalline residue was washed with *n*-hexane (100 mL), collected, and dried in vacuo (16.0 g, 81%). ^1H NMR (CD_2Cl_2, 298 K, ppm): δ 1.15 (s, 18H, Bu^t), 1.24 (s, 36H, Bu^t), 1.28 (s, 18H, Bu^t), 1.81 (m, 16H, THF), 3.36 (d, 4H, $J = 12.0$ Hz, CH_2), 3.57 (d, 4H, $J = 13.1$ Hz, CH_2), 3.67 (m, 16H, THF), 4.40 (d, 4H, $J = 13.1$ Hz, CH_2), 4.52 (d, 4H, $J = 12.0$ Hz, CH_2), 7.07 (s, 4H, Ar), 7.16 (s, 4H, Ar), 7.22 (s, 4H, Ar), 7.32 (s, 4H, Ar). Anal. Calcd. for **2**$\cdot$THF$_4$, $C_{104}H_{136}Nb_2O_{12}$: C, 70.80; H, 7.79. Found: C, 70.73; H, 8.11. Crystals suitable for X-ray analysis were grown in a saturated THF solution. Crystal data are reported in the Supporting Information.

(7) Procedure for **3**: Sodium (0.827 g, 36.0 mmol) was added, under argon, to a THF (500 mL) suspension of **2**$\cdot$THF$_4$ (31.74 g, 18.0 mmol). The reaction was stirred at room temperature for 2 days. The resulting dark green solution was filtered and evaporated to dryness. The solid residue was dried in vacuo, washed with *n*-hexane (200 mL), and dried again in vacuo for 10 h (25.9 g, 74%). ^1H NMR (C_4D_8O, 298 K, ppm): δ 1.15 (s, 36H, Bu^t), 3.08 (d, 4H, $J = 11.6$ Hz, CH_2), 4.79 (d, 4H, $J = 11.6$ Hz, CH_2), 7.0 (s, 8H, Ar). Anal. Calcd for **3**, $C_{112}H_{152}Na_2Nb_2O_{14}$: C, 68.82; H, 7.85. Found: C, 68.68; H, 7.80.

(8) For the preparation and crystal data, see the Supporting Information.

(9) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993; Chapters 9.3 and 9.4, and references therein.

(10) An accurate SQUID analysis between 1.9 and 320 K and at variable magnetic field indicates a rather high TIP (temperature-independent paramagnetism), typical for a singlet ground state but with near low-lying nonpopulated excited states.

(11) Procedure for **5**: Sodium (0.555 g, 24.1 mmol) was added, under argon, to a THF (250 mL) suspension of **2**$\cdot$THF$_4$ (21.3 g, 12.1 mmol). The reaction was stirred at room temperature for 2 days. The brown suspension became a dark solution which was filtered, degassed, saturated with nitrogen, and stirred at room temperature for 4 days. Volatiles were removed in vacuo, the yellow solid residue was washed with *n*-hexane (200 mL) and then collected and dried in vacuo (18.08 g, 76%). ^1H NMR (C_5D_5N, 298 K, ppm): δ 1.14 (s, 72H, Bu^t), 1.60 (m, 24H, THF), 3.12 (d, 8H, $J = 12.0$ Hz, CH_2), 3.64 (m, 24H, THF), 4.89 (d, 8H, $J = 12.0$ Hz, CH_2), 7.14 (s, 16H, Ar). Anal. Calcd for $[Nb_2\{calix[4]\text{-}(O)_4\}_2(\mu\text{-}N_2)Na_2(THF)_6]$, $C_{112}H_{152}N_2Na_2Nb_2O_{14}$: C, 67.85; H, 7.74; N, 1.41. Found: C, 67.44; H, 7.74; N, 1.41. When a THF solution of analytically pure **3** was saturated with N_2 and stirred at room temperature overnight, **5** was quantitatively formed. Crystals of complex **5** suitable for X-ray analysis were grown from a saturated benzene/diglyme solution, and each Na^+ is solvated by two diglyme molecules.

S0002-7863(97)02258-0 CCC: $15.00

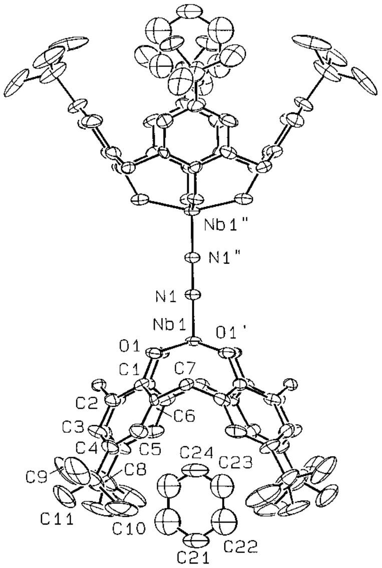

Figure 1. ORTEP drawing of complex 5 (30% probability ellipsoids). Selected bond distances (Å): Nb1−O1, 1.991(8); Nb1−N1, 1.748(12); N1−N1″, 1.390(17); O1−C1, 1.350(10). Bond angles (deg): O1−Nb1−N1, 102.9(3); O1−Nb1−O1′, 87.1(3); Nb1−O1−C1, 132.1(6); Nb1−N1−N1″, 180.0(-). Prime and double prime denote transformations of 0.5 - *y*, *x*, *z* and *x*, 0.5 − *y*, 0.5 − *z*, respectively. Disorder involving the guest benzene molecule has been omitted for clarity.

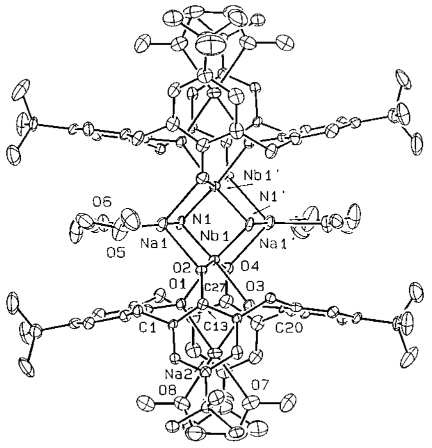

Figure 2. ORTEP drawing of complex 7 (50% probability ellipsoids). Selected bond distances (Å): Nb1−O1, 2.117(6); Nb1−O2, 2.067(6); Nb1−O3, 2.117(5); Nb1−O4, 2.084(6); Nb1−N1, 1.906(6); Nb1−N1′, 1.914(7); Na1−N1, 2.433(8). Bond angles (deg): N1−Nb1−N1′, 85.7(3); Nb1′−N1−Na1, 96.6(3); Nb1−N1−Na1, 97.1(3); Nb1−N1−Nb1′, 94.3(3). Prime denotes a transformations of −*x*, −*y*, −*z*.

The crystals of **5**[12] from diglyme consist of $[\{Nb(p\text{-}Bu^t\text{-}calixarene)\}_2(\mu\text{-}N_2)]^{2-}$ dianions (Figure 1), disordered $[Na(diglyme)_2]^+$ cations, and benzene hosted in the calixarene cavity. Each Nb calixarene unit possesses a crystallographically imposed C_4 symmetry, with the niobium displaced by 0.446(1) Å from the O_4 planar core. The Nb−N [1.748(12) Å][13] and the N−N [1.390(17) Å] distances support the presence in **5** of the four-electron-reduced hydrazido form of dinitrogen. This is indirectly supported by the reaction of **5** with PhCHO to give the corresponding azine[14] and the niobyl derivative **8**,[15] obtained also by reaction of **3** and **5** with O_2. The N−N distance is the longest ever found in an end-on bridging N_2[4] and is comparable to that in the hydrazido complexes.[16] The reducing power of the carbenoid Nb(III) in the active form **3** is displayed in the reaction with azobenzene, with the complete cleavage of the N═N and the formation of the terminal imido Nb complex **6**[17] [Nb═N, 1.758(15) Å; Nb−N−Ph, 175.5(15)°]. Only in a few other cases has complete cleavage been observed.[13c,e,18] The weak N−N single bond in **5**, reduced with Na, led to the nitride dimer complex **7**[19] (Figure 2).[20] The dimer has a C_i symmetry and a planar Nb_2N_2 core, with Nb···Nb and N···N separation of 2.801(1) and 2.598(8) Å, respectively. The nitrido[21] anion bridges the two Nb with an average distance of 1.910(7) Å and experiences a long-distance interaction with Na^+ at 2.433(8) Å.

The stepwise reduction of N_2 to nitride achieved using the Nb calix[4]arene fragment has several analogies with the pioneering work by Cummins, who used a d^3 Mo(III) trisamido complex.[2]

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Supporting Information Available: Crystal data for **2** and **4**−**8**; preparation of **4** and **6**; and description of the structures, SCHAKAL drawings, tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **5** and **7** (19 pages). See any current masthead page for ordering and Internet access instructions.

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(12) Crystal data for **5**: $C_{88}H_{104}N_2Nb_2O_8{\cdot}2C_{12}H_{28}NaO_6{\cdot}2C_6H_6$, $M = 2242.5$, tetragonal, space group P_4/nnc, $a = 12.950(2)$ Å, $c = 40.164(5)$ Å, $V = 6735.6(17)$ Å^3, $Z = 2$, $D_{calcd} = 1.106$ g/cm^3, $F(000) = 2388$, λ(Cu Kα) = 1.54178 Å, μ(Cu Kα) = 19.29 cm^{-1}: crystal dimensions 0.12 × 0.35 × 0.52 mm. The structure was solved by the heavy atom method and anisotropically refined for all non-H atoms except for those affected by disorder. For 837 unique observed reflections $[I > 2\alpha(I)]$ collected at $T = 295$ K on a Rigaku AFC6S diffractometer (6° $< 2\theta <$ 140°) and corrected for absorption, the final R is 0.070 ($wR_2 = 0.219$ for the 1936 reflections having $I > 0$ used in the refinement).

(13) (a) Green, M. L. H.; James, J. T.; Saunders: J. F.; Souter, J. *J. Chem. Soc., Dalton Trans.* **1997**, 1281. (b) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988; Chapter 5, p 179. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 4749. (d) Tan, L. S.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 1744. (e) Lockwood, M. A.; Fanwick, P. E.; Eisenstein, O.; Rothwell, I. P. *J. Am. Chem. Soc.* **1996**, *118*, 2762.

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(15) ^{1}H NMR (C_5H_5N, 298 K, ppm): δ 1.20 (s, 36H, Bu^t), 1.59 (m, 16H, THF), 3.40 (d, 4H, J = 11.7 Hz, CH_2), 3.64 (m, 16H, THF), 5.25 (d, 4H, J = 11.7 Hz, CH_2), 7.28 (s, 8H, Ar). Crystal data are reported in the Supporting Information.

(16) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760.

(17) For the preparation and crystal data, see the Supporting Information.

(18) Wiberg, N.; Häring, H.-W.; Schubert, U. *Z. Naturforsch.* **1978**, *33B*, 1365. Canich, J. A. M.; Cotton, F. A.; Duraj, S. A. Roth, W. J. *Polyhedron* **1986**, *5*, 895.

(19) Procedure for **7**: Sodium (0.17 g, 7.39 mmol) was added to a THF (300 mL) solution of $[Nb_2\{calix[4]\text{-}(O)_4\}_2(\mu{-}N_2)Na_2(THF)_6]$ (7.22 g, 3.64 mmol), and the reaction was stirred at room temperature for 4 days under Ar. A white crystalline solid precipitated and was extracted with the mother liquor for 4 h. A white solid again precipitated which was collected and dried in vacuo (4.60 g, 51%). Anal. Calcd for $[Nb_2(\mu_3\text{-}N_2)\{calix[4]\text{-}(O)_4\}_2(Na)_2(THF)_{12}]$, $C_{136}H_{200}N_2Na_4Nb_2O_{20}$: C, 66.36; H, 8.21; N, 1.14. Found: C, 66.45; H, 8.09; N, 1.12. ^{1}H NMR (C_5D_5N, 298 K, ppm): δ 1.12 (s, 72H, Bu^t), 1.60 (m, 48H, THF), 3.13 (d, 8H, J = 11.7 Hz, CH_2), 3.64 (m, 48H, THF), 5.29 (d, 8H, J = 11.7 Hz, CH_2), 7.01 (s, 16H, Ar). Crystals of **7** for X-ray analysis were obtained from DME/chlorobenzene, which remains as crystallization solvent.

(20) Crystal data for **7**: $C_{104}H_{144}N_2Na_4Nb_2O_{16}{\cdot}6C_6H_5Cl$, $M = 2631.4$, triclinic, space group, $a = 17.086(3)$ Å, $b = 17.767(3)$ Å, $c = 12.709(2)$ Å, $\alpha = 101.49(2)°$, $\beta = 104.63(1)°$, $\gamma = 66.10(1)°$, $V = 3392.3(10)$ Å3, $Z = 1$, $D_{calcd} = 1.288$ g/cm^3, $F(000) = 1384$, λ(Cu Kα) = 1.54178 Å, μ(Cu Kα) = 31.26 cm^{-1}; crystal dimensions 0.23 × 0.30 × 0.52 mm. The structure was solved by the heavy atom method and anisotropically refined for all non-H atoms except for those affected by disorder. For 5963 unique observed reflections $[I > 2\sigma(I)]$ collected at $T = 143$ K on a Rigaku AFC6S diffractometer (6° $< 2\theta <$ 140°) and corrected for absorption, the final R is 0.067 ($wR_2 = 0.202$ for the 10035 reflections having $I > 0$ used in the refinement).

(21) For terminal nitrides, see: (a) ref 2. (b) Herrmann, W. A.; Bogdanovic, S.; Poli, R.; Priermeier, T. *J. Am. Chem. Soc.* **1994**, *116*, 4989. (c) Caulton, K. G.; Chisholm, M. H.; Doherty, S.; Folting, K. *Organometallics* **1995**, *16*, 2585. (d) Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 4999. (e) Odom, A. L.; Cummins, C. C. *Organometallics* **1996**, *15*, 898.