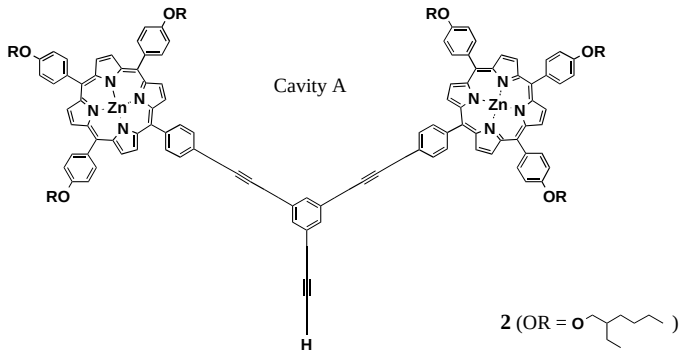


estimated to be 1.18 nm, which is comparable with the size of $C_{60}$ (diameter, 1.00 nm).[12] One can thus consider that cavity B is acting as a real binding site.

In conclusion, the present study demonstrated that the dendritic receptor **1** binds three $C_{60}$ guests in the positive allosteric manner with high Hill coefficient of 2.8. With the aid of this effect, the *K* value is considerably enhanced. In addition, the findings have important implications because molecular recognition can be coupled with the control of various chemical and physical functions inherent to the porphyrin–fullerene interaction, such as solubilization of $C_{60}$ in polar solvents, photochemical electron or energy transfer as a photosynthetic model, electrochemical redox reactions, etc.

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## Dinitrogen-Bond Cleavage in a Niobium Complex Supported by a Tridentate Aryloxide Ligand

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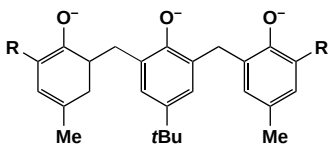
The efficient activation of dinitrogen under mild conditions is a challenging topic in chemistry because of its important applications. Although dinitrogen complexes of almost transition metals have been prepared,[1] there are few examples of well-characterized transition-metal compounds which are capable of cleaving the N≡N bond.[2] As part of studies aimed at developing new ancillary ligands to support reactive metal centers, we have found it attractive to employ linked aryloxide ligands (R-$L^{3-}$; R = *t*Bu, Me; Scheme 1),[3, 4, 5] to determine complex geometry and to limit ligand mobility. Furthermore, their steric size can be easily regulated by substituents at *ortho* positions of the outer aryloxides. We chose to investigate the chemistry of niobium complexes with the R-$L^{3-}$ ligands in dinitrogen activation. Herein we describe the reductive N≡N-bond cleavage by the combination of $LiBHEt_3$ and a niobium complex supported by a tridentate aryloxide ligand.




Scheme 1. Ligands, R-$L^{3-}$ (R = *t*Bu, Me).

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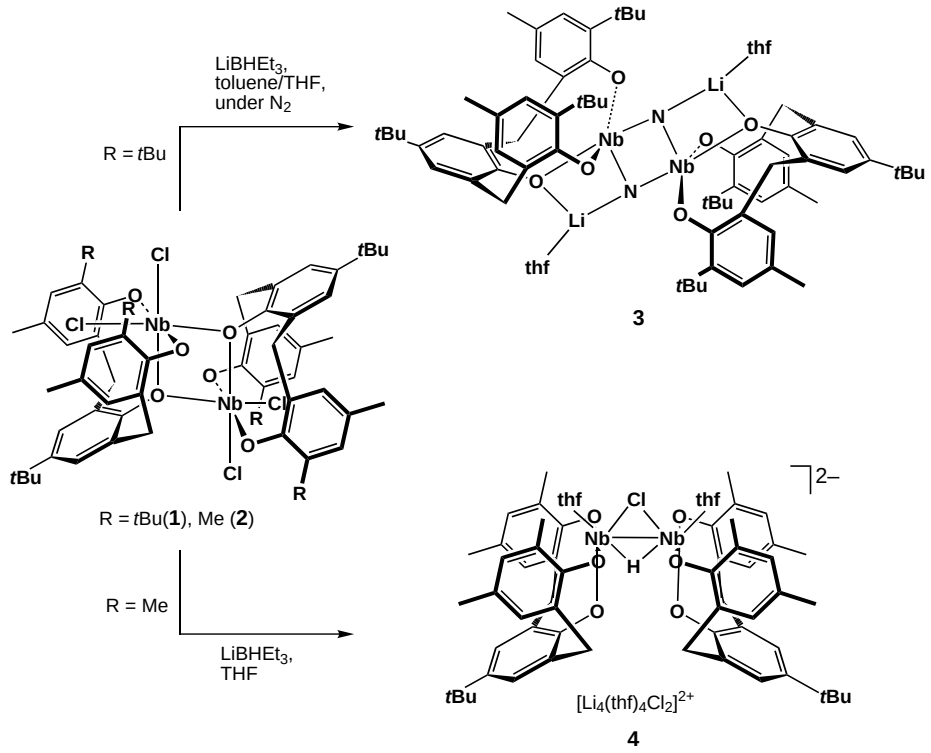


Scheme 2. Synthesis of **3** and **4**.

Addition of 6 equivalent of $LiBHEt_3$ in THF to a toluene solution of $[\{Nb(t\text{Bu-L})Cl_2\}_2]$ (**1**)[6] at $-78\,^{\circ}C$ under $N_2$ gave a red solution. When the solution was stirred at room temperature, the solution gradually turned brown. After removal of an insoluble brown powder, $[\{Nb(t\text{Bu-L})(\mu\text{-N})Li(thf)\}_2]$ (**3**; Scheme 2) was isolated as yellow crystals in 41 % yield by the addition of hexane. On the other hand, the reaction carried out under argon resulted in an uncharacterized material. The combustion analysis and spectroscopic data of **3** is in agreement with the formula. The $^{15}N$ NMR spectrum of the isotopically enriched compound $[\{Nb(t\text{Bu-L})(\mu\text{-}^{15}N)Li(thf)\}_2]$ (**3**-$^{15}N$), analogously prepared under an atmosphere of $^{15}N_2$, displays a single resonance peak at $\delta = 312$ ppm in the $^{15}N$ NMR spectrum. This result unambiguously confirms that the bridging ligands of **3** originate from $N_2$.

The X-ray diffraction analysis reveals that **3** is dimeric with two bridging nitrides (Figure 1).[7] The $t$Bu-$L^{3-}$ ligands bind to the niobium atoms in a facial manner. There are two lithium cations, each bridging the central aryloxide and the nitrogen atom. The trigonal-planar coordination around lithium centers is completed by thf. Each niobium atom in the centrosymmetric dimer is five-coordinate in a geometry that approximates a trigonal bypiramid, with the central aryloxide of $t$Bu-$L^{3-}$ and a bridging nitride unit occupying the apical sites. The bridging nitrides are arranged in an unsymmetrical fashion, with the axial Nb–N′ bond of 1.935(3) Å being slightly longer than the equatorial Nb–N bond of 1.892(3) Å.[2b, 2d, 8] Two nitrogen atoms are separated by 2.569(5) Å, indicative of the complete cleavage of the N≡N bond. The short Nb···Nb separation of 2.837(4) Å is a result of the presence of two bridging nitride groups.

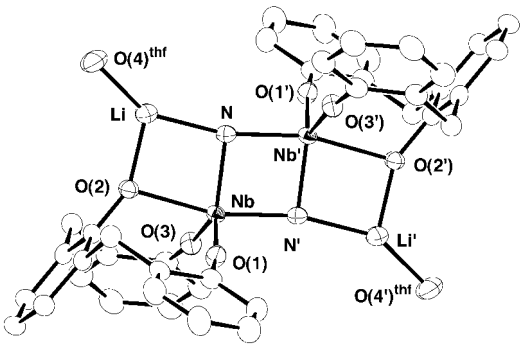


Figure 1. Molecular structure of **3**. Methyl and *tert*-butyl groups of $t$Bu-$L^{3-}$ ligands and the thf groups (except for the oxygen atom) have been omitted for clarity.

The use of Me-$L^{3-}$ instead of $t$Bu-$L^{3-}$ ions introduced a significant modification in the reactivity pattern of niobium complexes. The analogous reaction of $[\{Nb(\text{Me-L})Cl_2\}_2]$ (**2**) with $LiBHEt_3$ in THF gave $[\{Nb_2(\text{Me-L})_2(\mu\text{-H})(\mu\text{-Cl})(thf)_2\}\{Li_4(thf)_4Cl_2\}]$(**4**; Scheme 2) as green crystals in 73 % yield. Compound **4** is diamagnetic, and its formulation was confirmed by spectroscopic data and X-ray analysis. Figure 2 presents the solid state structure of **4**, where a crystallographically imposed mirror plane passes through the molecule.[9] A striking feature of the structure is the presence of a $[\{Nb(\text{Me-L})(thf)\}_2(\mu\text{-Cl})(\mu\text{-H})]^{2-}$ dimer, in which each Nb center possesses an octahedral geometry (if the Nb–Nb bond is ignored). The two Me-$L^{3-}$ ligands are arranged in a *syn* configuration. The

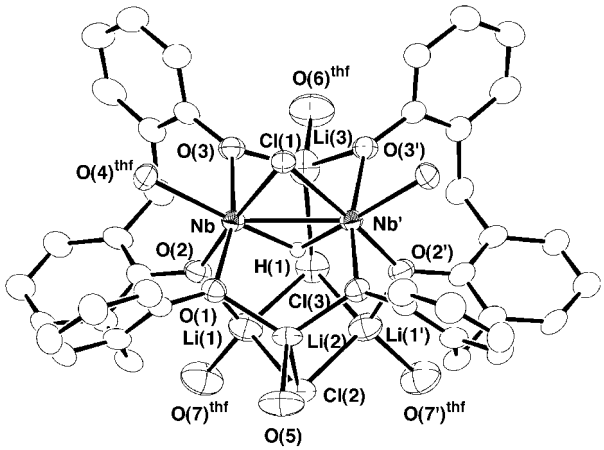


Figure 2. Structure of **4**. Methyl and *tert*-butyl groups of Me-$L^{3-}$ ligands and the thf groups (except for the oxygen atom) have been omitted for clarity.

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dimeric $[\{Nb(Me\text{-}L)(thf)\}_2(\mu\text{-}Cl)(\mu\text{-}H)]^{2-}$ unit carries four lithium atoms coordinating at aryloxide units and two chlorine atoms bridging three lithium atoms. Taking account into the observed diamagnetism of **4**, the short Nb–Nb separation of 2.647(1) Å suggests the presence of the Nb–Nb double bond.[10] Although determination of the position of the hydride ligand from X-ray data alone is difficult, the Fourier map yielded a residual peak on the side of the Nb – Nb vector, opposite that of the bridging Cl(1) atom, which could be assigned to the bridging hydride ligand (Nb–H(1) 1.80 Å).

The $^1$H NMR spectrum of **4** in $C_6D_6$ is consistent with its solid-state structure. The resonance signal for the bridging hydride ligand is observed as a broad signal at $\delta = -1.1$ ppm. When **4** was dissolved into $CDCl_3$, the signal at $\delta = -1.1$ ppm disappeared and the formation of **2** was indicated. While no terminal Nb–H stretching band was observed in the IR spectrum, the assignment of the bridging hydride ligand was impossible because of overlapping peaks. An attempt to prepare a dihydride-bridging dimer by the reaction of **4** with $LiBHEt_3$ in THF was unsuccessful. The $Nb_2(\mu\text{-Cl})$ unit remained intact, and **4** was recovered from the reaction mixture.

In conclusion this work clearly shows that each $R\text{-}L^{3-}$ ligand behaves in a very distinct manner with respect to dinitrogen activation and metal – metal interaction. In light of the isolation of **4**, the formation of **3** presumably proceeds via an $Nb^{III}(\mu\text{-H})_2Nb^{III}$ dimer. This intermediate could bind and cleave $N_2$ concomitant with the reductive elimination of $H_2$ to produce **3**, because the loss of $H_2$ to generate a dinitrogen complex is known.[11] Further study to isolate such a species is currently underway.

### *Experimental Section*

All manipulations were performed under $N_2$ using standard Schlenk techniques and dried, deoxygenated solvents.

**3**: A 100-mL flask was charged with **1** (1.10 g, 0.83 mmol), $LiBHEt_3$ (1M in THF; 5.0 mL, 5.0 mmol), and toluene (60 mL) at $-78\,^\circ$C. Upon stirring the mixture at room temperature for 28 h, a brown solution was obtained. After centrifugation to remove insoluble material, the solution was layered with hexane to afford **3** as yellow crystals (0.57 g, 41 %). $^1$H NMR (500 MHz, [D$_8$]THF): $\delta = 1.40$ (s, 18H; *t*Bu), 1.43 (s, 36H; *t*Bu), 2.31 (s, 12H; Me), 4.62 (d, $J = 12.7$ Hz, 4H; $CH_2$), 5.54 (d, $J = 12.7$ Hz, 4H; $CH_2$), 6.84 (s, 4H; Ph), 6.86 (s, 4H; Ph), 7.00 ppm (s, 4H, Ph); $^{15}$N NMR (50.55 MHz,[D$_8$]THF, $CH_3NO_2$ external standard): $\delta = 312$ ppm; elemental analysis calcd (%) for $C_{90}H_{118}O_8N_2Li_2Nb_2$: C 69.49, H 7.65, N 1.80; found: C 69.12, H 7.59, N 1.55.

**4**: A 100-mL flask was charged with **2** (0.94 g, 0.81 mmol), $LiBHEt_3$ (1M in THF; 4.9 mL, 4.9 mmol), and THF (50 mL) at $-78\,^\circ$C. Upon stirring the mixture at room temperature for 32 h, a green solution was obtained. Concentration and subsequent cooling of the solution to $-30\,^\circ$C gave **4** as green crystals (1.06 g, 73 %). $^1$H NMR ($C_6D_6$): $\delta = -1.1$ (br, 1H; Nb-H-Nb), 1.27 (s, 18H; *t*Bu), 1.3 (br; thf), 2.21 (s, 6H; Me), 2.93 (s, 6H; Me), 3.39 (d, $J = 12$ Hz, 4H; $CH_2$), 3.6 (br; thf), 5.73 (d, $J = 12$ Hz, 4H; $CH_2$), 6.83 (s, 4H; Ph), 7.09 (s, 4H; Ph), 7.19 ppm (s, 4H, Ph); elemental analysis calcd (%) for $C_{92}H_{135}O_{15}Cl_3Li_4Nb_2$: C 61.36, H 7.56; found: C 60.44, H 7.38.

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[7] a) Crystal data for **3**: $C_{76}H_{102}N_2O_8Li_2Nb_2 \cdot 2C_7H_8$ ($M_r = 1555.62$); crystal size $0.35 \times 0.20 \times 0.20$ mm, monoclinic, $P2_1/c$ (no. 14), $a = 12.984(1)$, $b = 18.647(2)$, $c = 17.567(2)$ Å, $\beta = 104.706(5)^\circ$, $V = 4113.7(7)$ Å$^3$, $\rho_{calcd} = 1.256$ g cm$^{-3}$, $Z = 2$, $\mu(Mo_{K\alpha}) = 3.34$ cm$^{-1}$, 32459 measured, 9094 unique, 528 variables, GOF = 1.04, $R1 = 0.044$, $wR_2 = 0.145$; b) Diffraction data of **3** and **4** were collected at $-100\,^\circ$C on a Rigaku Mercury system equipped with a CCD detector ($Mo_{K\alpha}$ radiation, $\lambda = 0.71070$ Å; graphite-monochromated). The structures of **3** and **4** were solved by direct methods and refined by full-matrix least-squares on $F^2$ by using the CrystalStructure software package. All non-hydrogen atom were refined anisotropically, and hydrogen atoms were located at calculated positions. CCDC-175198 (**3**) and CCDC-175199 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[9] Crystal data for **4**: $C_{80}H_{111}O_{12}Cl_3Li_4Nb_2 \cdot 3C_4H_8O$ ($M_r = 1801.01$); crystal size $0.25 \times 0.10 \times 0.05$ mm, orthorhombic, *Pnma* (no. 62), $a = 17.657(5)$, $b = 26.656(8)$, $c = 20.010(6)$ Å, $V = 9418(4)$ Å$^3$, $\rho_{calcd} = 1.270$ g cm$^{-3}$, $Z = 4$, $\mu(Mo_{K\alpha}) = 3.88$ cm$^{-1}$, 74544 measured, 11010 unique, 533 variables, GOF = 1.08, $R1 = 0.057$, $wR_2 = 0.166$.[7b] The *t*Bu group and one of the thf molecules were disordered with 70/30 and 60/40 site occupancies, respectively.

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