

# The reduction of Nb<sub>2</sub>Cl<sub>6</sub>(tmeda)<sub>2</sub> by R<sub>2</sub>NLi. Formation of a diamagnetic niobium(II) cluster with short Nb–Nb triple bond and amide C–N bond cleavage

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Reduction of trivalent Nb<sub>2</sub>Cl<sub>6</sub>(tmeda)<sub>2</sub> with either lithium diisopropylamide or *n*-butyllithium yields a novel Nb<sup>II</sup> cluster which performs oxidative addition into the amide C–N bond.

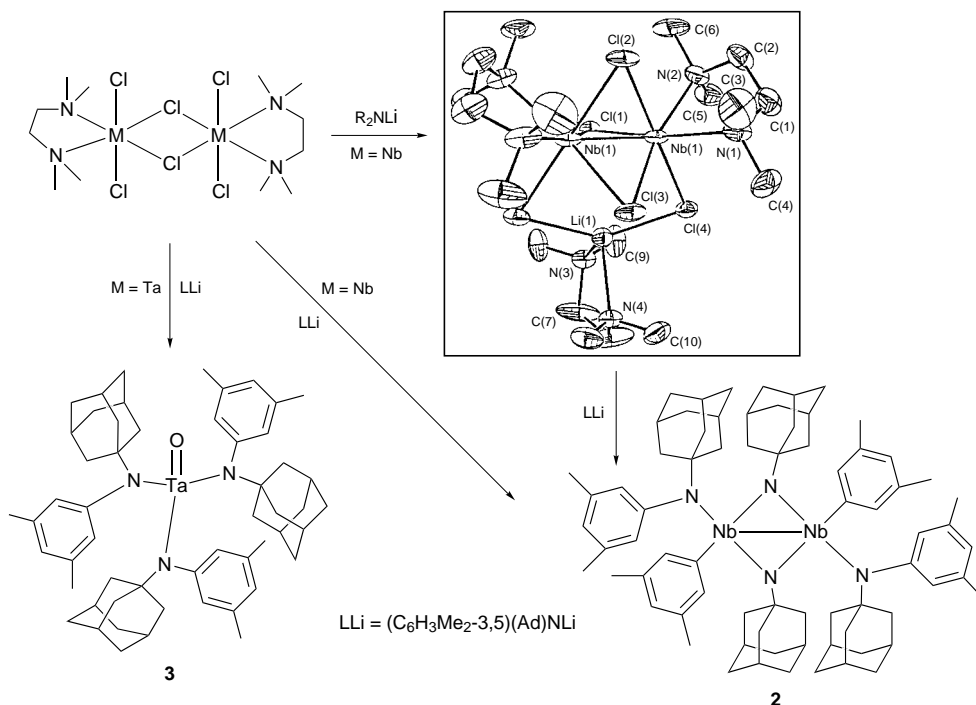
Halide complexes of divalent Nb and Ta are particularly rare and limited to a few di- and poly-nuclear structures of halide derivatives mainly bridged by tetrahydrothiophene (THT) ligands.<sup>1</sup> The M–M triple bonds in these species are surprisingly long and thus to evaluate their properties it is important to prepare a variety of multiply bonded systems with the greatest possible diversity of ligand environments.

This work was prompted by the simple idea that low-valent niobium and tantalum amides may be able to form polynuclear structures with or without bridging ligands. The choice of these anions as supporting ligands was advised by their well established ability to stabilize highly reactive medium valent early transition metals.<sup>2</sup> With the dual purpose of bypassing the difficulties arising from the treatment of MCl<sub>5</sub> (M = Nb, Ta) starting materials with anionic amides<sup>3</sup> and possible complications arising from their subsequent reduction, and in an attempt to gain some insight into the stability of trivalent Nb and Ta amide, we have now reacted the dinuclear [MCl<sub>3</sub>(tmeda)]<sub>2</sub>

(M = Nb, Ta; tmeda = *N,N,N',N'*-tetramethylethylenediamine)<sup>4</sup> with R<sub>2</sub>NLi derivatives. Herein we describe our preliminary findings.

A stoichiometric 1:3 ratio of Nb to amide, as well as an extended reflux in thf, was always necessary to complete the reactions of [NbCl<sub>3</sub>(tmeda)]<sub>2</sub> with RR'NM' [RR'NM' = Ph<sub>2</sub>NNa, Pr<sub>2</sub>NLi, (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-3,5)(Ad)NLi (Ad = adamantyl)] and to avoid the presence of unreacted starting materials in the reaction mixtures. However, in the particular case of LDA (lithium diisopropylamide) the reaction was completed in a few hours at room temp. After suitable work-up, well formed, dark-brown, and air-sensitive crystals of a new diamagnetic product were isolated in poor yield. The IR and the NMR of the crystalline product clearly indicated that the complex contained two non-equivalent tmeda ligands. The presence of lithium, suggested by qualitative flame tests, was confirmed by <sup>7</sup>Li NMR spectroscopy. Combustion analysis data were in agreement with the formulation (tmeda)<sub>3</sub>Nb<sub>2</sub>Cl<sub>5</sub>Li **1**. An X-ray structure confirmed the formula and elucidated the molecular connectivity (Fig. 1).<sup>†</sup>

The crystal structure of **1** provides a rare example of a dinuclear niobium(II) complex. The diamagnetism and the very short Nb–Nb distance [Nb–Nb 2.4001(5) Å], suggest the



**Fig. 1** Selected bond distances (Å) and angles (°) for complex **1**: Nb(1)–Nb(1a) 2.4001(5), Nb(1)–Li(1) 3.217(8), Nb(1)–Cl(1) 2.5712(9), Nb(1)–Cl(2) 2.579(1), Nb(1)–Cl(3) 2.569(1), Nb(1)–Cl(4) 2.5583(9), Nb(1)–N(1) 2.390(2), Nb(1)–N(2) 2.366(3), Li(1)–Cl(4) 2.489(3), Li(1)–Cl(3) 2.840(8), Li(1)–Cl(1) 3.031(9), Li(1)–N(3) 2.199(9), Li(1)–N(4) 2.162(9), Cl(1)–Nb(1)–Cl(2) 95.90(3), Cl(1)–Nb(1)–Cl(3) 108.13(3), Cl(1)–Nb(1)–Cl(4) 84.39(3), Cl(1)–Nb(1)–N(1) 165.65(8), Cl(1)–Nb(1)–N(2) 85.83(7), Cl(2)–Nb(1)–Cl(3) 95.28(4), Cl(2)–Nb(1)–Cl(4) 84.16(3), Cl(2)–Nb(1)–N(1) 86.24(8), Cl(2)–Nb(1)–N(2) 85.45(8), Cl(3)–Nb(1)–Cl(4) 84.16(3), Cl(3)–Nb(1)–N(1) 85.73(8), Cl(3)–Nb(1)–N(2) 165.82(7), Cl(4)–Nb(1)–N(1) 93.60(8), Cl(4)–Nb(1)–N(2) 95.06(8), N(1)–Nb(1)–N(2) 80.2(1).

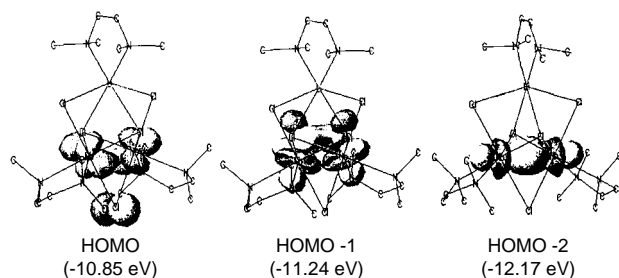


Fig. 2 Pictorial view of the frontier orbitals of **1**

presence of a Nb–Nb triple bond.<sup>5</sup> However, the shortness of the intermetallic distance contrasts with those of the few previously reported divalent diniobium or ditantalum THF bridged complexes,<sup>1</sup> whose unusually long M–M distances were ascribed to an intrinsic weakness of the metal–metal bonds.<sup>1b</sup> Theoretical calculations carried out on the atomic crystallographic coordinates of **1** show that the three highest occupied molecular orbitals are mainly Nb–Nb centered with a metal atom contribution of predominantly d-orbital character and a minor but significant contribution from the p orbitals of the bridging chlorine atoms. The HOMO–LUMO gap (0.53 eV) is rather small yet sufficient to account for the observed diamagnetism in solution. The three MOs are formed by the overlap of hybrid atomic orbitals of the two niobium atoms. The shape of the HOMO (Fig. 2) is reminiscent of a M–M  $\delta$  bond while the LUMO (–10.32 eV) is the corresponding out-of-phase combination. The next occupied molecular orbital, located at –11.24 eV is also M–M centered and has some  $\pi$ -bond character, while the third next orbital (–12.17 eV) is a regular  $\sigma$  bond lying symmetrically on the intermetallic vector. At this stage is not clear which factor (electronic or steric) is responsible for the short Nb–Nb distance. Certainly, we cannot rule out the possibility that the lithium cation may ultimately determine the intermetallic distance by bringing together the two vertices of the two octahedra.

The reduction of the metal center to the divalent state by LDA implies that the amide acted as a strong reductant.<sup>6</sup> Thus, it was possible to prepare **1** in higher yield by simply reacting  $[\text{NbCl}_3(\text{tmeda})]_2$  with 2 equiv. of  $\text{Bu}^n\text{Li}$  in ether and in the presence of a small excess of tmeda. Even though the ability of amides to act as reductants is documented in the literature,<sup>7</sup> the fact that the same reaction with  $\text{Ph}_2\text{NNa}$  (instead of LDA) gave the tetravalent derivative  $(\text{Ph}_2\text{N})_4\text{Nb}$  (45%)<sup>8</sup> suggests that the reduction of the metal center during the formation of **1** might occur through the disproportionation of an unstable niobium(III) intermediate. In addition, the reaction of  $[\text{NbCl}_3(\text{tmeda})]_2$  with  $(\text{C}_6\text{H}_3\text{Me}_2-3,5)(\text{Ad})\text{NLi}$  yielded the tetravalent, dinuclear and diamagnetic  $[(\text{C}_6\text{H}_3\text{Me}_2-3,5)(\text{Ad})\text{N}]_2\text{Nb}(3,5-\text{Me}_2\text{Ph})_2(\mu\text{-NAd})_2 \cdot 2\text{Et}_2\text{O}$  **2** (Fig. 1).<sup>†</sup> However, this product is likely to be originated by the further reaction of **1** with the lithium amide (the reaction requires reflux in thf for several hours in this case) to form a transient  $[(\text{C}_6\text{H}_3\text{Me}_2-3,5)(\text{Ad})\text{N}]_2\text{Nb}$  species which generates **2** via oxidative addition into the C–N bond of the amide function.<sup>9</sup> Accordingly, direct reaction of **1** with 2 equiv. of  $(\text{C}_6\text{H}_3\text{Me}_2-3,5)(\text{Ad})\text{NLi}$  also gave complex **2** in crystalline form.

The reaction of  $[\text{TaCl}_3(\text{tmeda})]_2$  with amides took a different pathway. While the majority of these reactions led to intractable materials, in the case of the reaction with  $(\text{C}_6\text{H}_3\text{Me}_2-3,5)(\text{Ad})\text{NLi}$  the pentavalent  $[(\text{C}_6\text{H}_3\text{Me}_2-3,5)(\text{Ad})\text{N}]_3\text{Ta}(\text{O})$  **3** was isolated and characterized.<sup>‡</sup> The complex is likely to be originated by the reaction of the initially formed  $[(\text{C}_6\text{H}_3\text{Me}_2-3,5)(\text{Ad})\text{N}]_3\text{Ta}$  species with thf since reactions carried out in different solvent led to different results. This hypothetical intermediate obviously possesses a greater stability with respect to the niobium analogue and performs a two-electron reduction

of thf. Accordingly, significant amounts of  $\text{CH}_4$  and  $\text{CH}_3\text{CH}_3$  (27 and 31%, respectively based on Ta) were recovered from the reaction mixture (Toepler pump and GC combined experiments).

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## Footnotes and References

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† Crystal data:  $\text{C}_{18}\text{H}_{48}\text{LiCl}_5\text{N}_6\text{Nb}_2$  **1**,  $M = 718.64$ , orthorhombic, space group  $\text{Cmc}21$ ,  $a = 15.2097(2)$ ,  $b = 16.8896(2)$ ,  $c = 12.0285(1)$  Å,  $U = 3089.95(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.545$  g cm<sup>-3</sup>,  $F(000) = 1471.49$ ,  $\mu = 11.9$  cm<sup>-1</sup>,  $T = -145$  °C,  $R = 0.026$ ,  $R_w = 0.031$ , GOF = 1.01 for 196 parameters and 2972 reflections out of 3508 unique collected with a Siemens CCD diffractometer.  $\text{C}_{40}\text{H}_{58}\text{N}_2\text{NbO}$  **2**,  $M = 675.81$ , monoclinic, space group  $\text{P}2_1/c$ ,  $a = 12.5969(2)$ ,  $b = 14.3835(1)$ ,  $c = 20.3103(3)$  Å,  $\beta = 104.223(1)^\circ$ ,  $U = 3567.17(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.258$  g cm<sup>-3</sup>,  $F(000) = 1436.34$ ,  $\mu = 3.7$  cm<sup>-1</sup>,  $T = -145$  °C,  $R = 0.045$ ,  $R_w = 0.057$ , GOF = 1.05 for 397 parameters and 6960 reflections out of 9089 unique collected with a Siemens CCD diffractometer.  $\text{C}_{64}\text{H}_{95}\text{N}_3\text{O}_2\text{Ta}$  **3**,  $M = 1119.41$ , monoclinic, space group  $\text{P}2_1/n$ ,  $a = 14.2622(2)$ ,  $b = 25.3107(1)$ ,  $c = 16.1753(2)$  Å,  $\beta = 101.706(3)$ ,  $U = 5717.6(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.300$  g cm<sup>-3</sup>,  $F(000) = 2355.36$ ,  $\mu = 1.96$  cm<sup>-1</sup>,  $T = -165$  °C,  $R = 0.033$ ,  $R_w = 0.041$ , GOF = 1.41 for 641 parameters and 11 040 reflections out of 14 513 unique collected with a Siemens CCD diffractometer. CCDC/602.

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