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Niobium-nitrides derived from nitrogen splitting†

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Cite this: *Chem. Commun.*, 2015, **51**, 3526

Received 30th November 2014,
Accepted 6th January 2015

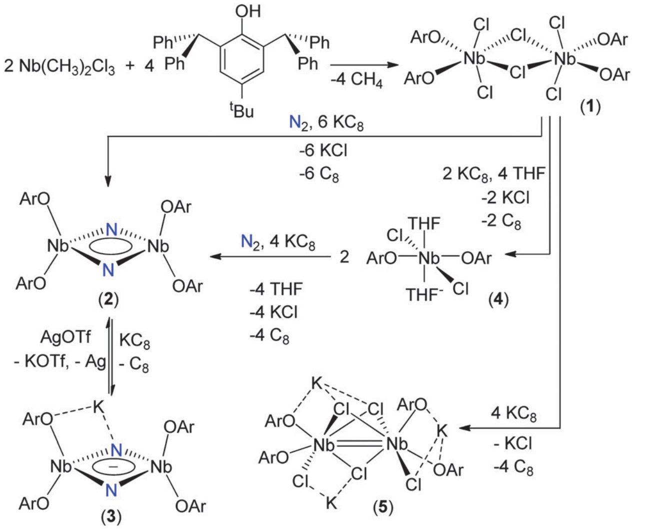
DOI: 10.1039/c4cc09563d

www.rsc.org/chemcomm

The easy-to-prepare Nb(V) aryloxide complex $[(ArO)_2Nb(\mu\text{-}Cl)Cl_2]_2$ (OAr = 2,6-bis(diphenylmethyl)-4-*tert*-butylphenoxide) is a precursor to both Nb(IV), [*trans*-$(ArO)_2NbCl_2(THF)_2$], and Nb(III), $K_3[(ArO)_4Nb_2(\mu\text{-}Cl)_3Cl_2]$, molecules. The Nb(IV) and (V) complexes readily split atmospheric nitrogen at room temperature and 1 atmosphere, under reducing conditions, to produce the low-coordinate nitride dimer $[(ArO)_2Nb(\mu\text{-}N)]_2$ and its radical anion, $K[(ArO)_2Nb(\mu\text{-}N)]_2$.

Activating and splitting dinitrogen, the most abundant gas in our atmosphere, is an important transformation that holds enormous promise in the conversion of this inert molecule into more value added compounds or materials.[1] Although early transition metals (groups 4–6)[3–10] are well-known to bind and reduce the bond order of N_2, there is still enormous interest in discovering other, well-defined systems[1] that can completely split this strong bond, having a BDE of 225 kcal mol^{-1}.[1] Notably, catalytic systems (with well-defined molecules) have been developed.[2] We were particular interested in exploring the chemistry of group 5 metals, especially niobium complexes supported with thermally robust and sterically hindered aryloxide ligands since these mimic to some extent the role of the metal in oxide supported surfaces.[3,8,10] In this regard, Kawaguchi has taken advantage of a tridentate aryloxide scaffold to further functionalize N_2 into NH_3, ureate, isocyanate, and imides[8b] while Floriani[3] and Sita[6b] have isolated key intermediates along the N≡N bond splitting pathway. Chirik has used CO and H_2 reagents among other reductants to promote N_2 splitting with group 4 metals.[9]

Inspired by some of the alkoxide chemistry by Rothwell,[11] Floriani,[3] and more recently Kawaguchi,[8] we set out to prepare niobium complexes supported by the sterically encumbering and highly arylated aryloxide ligand, 2,6-bis(diphenylmethyl)-4-*tert*-butylphenoxide.[12] This alkoxide can be obtained in a day, on a 0.25 kilogram preparative scale, and from it the dark-red niobium precursor, $[(ArO)_2Nb(\mu\text{-}Cl)Cl_2]_2$ (**1**), can be readily synthesized in 93% yield by the straightforward protonolysis of $[Nb(CH_3)_2Cl_3]$ with two equivalents of HOAr (Scheme 1). Despite the large steric encumbrance provided by the aryloxide, complex **1** exists as a dimer in the solid-state where each niobium occupies a distorted octahedral geometry.† We demonstrate here that compound **1** serves as an entry point to Nb(IV) and Nb(III) complexes, and both Nb(IV) and (V) are competent at cleaving molecular nitrogen's triple bond at 25 °C under reducing conditions, while the Nb(III) species is not. Lastly, we validate that these nitride complexes, derived from N_2 splitting, are capable of producing NH_4Cl when treated with anhydrous $HCl(Et_2O)$.



Scheme 1 Synthesis of complexes **1–5**, where –OAr represents 2,6-bis-(diphenylmethyl)-4-*tert*-butylphenoxide.

When the dark-red colored complex **1** is added an excess of KC_8 (*ca.* 6 equivalents) in a toluene–THF mixture and stirred at

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† Electronic supplementary information (ESI) available: Experimental procedures, NMR spectrum, and crystallographic information (CIF). Compounds **1–5**. CCDC 1032675–1032679. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc09563d

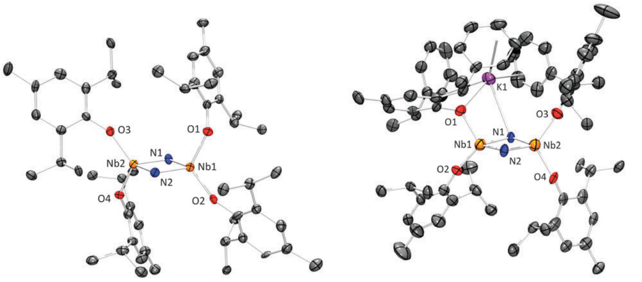

Fig. 1 Molecular structures of **2** (left) and **3** (right) with thermal ellipsoids at the 50% probability level. Carbons of the $-{}^{t}$Bu and non-interacting $-CHPh_2$ groups as well as all hydrogens have been omitted for clarity.

25 °C under a N_2 atmosphere over 10 hours, several color changes occur initially in the sequence of yellow, green, orange, yellow-brown and ultimately to form a orange-brown suspension. Filtration of the insoluble products yields an orange-brown filtrate from which yellow powder can be obtained in 38% yield (^{1}H NMR spectrum reveals formation of this new product in >60% yield). From the remaining filtrate, another product can be crystallized as purple single crystals albeit in low yield (<5%). The yellow product displays sharp resonances in the ^{1}H NMR spectrum, recorded in C_6D_6, consistent with a diamagnetic species having a single chemical environment for the –OAr ligand. An X-ray diffraction study performed on a yellow single-crystal, grown from cooling a concentrated toluene solution layered with pentane to −35 °C, reveals this species to be a nitride dimer of the chemical formula $[(ArO)_2Nb(\mu\text{-}N)]_2$ (**2**) (Fig. 1, Scheme 1). The solid-state analysis exposes a nearly symmetric diamond core structure where each niobium exists in a pseudo-tetrahedral chemical environment (τ_4 = 0.89 and 0.92).[13] The niobium metals are bridged through two nitride ligands with Nb–N distances ranging from 1.876(6)–1.900(6) Å. These distances are notably longer than that of a terminally bound nitride ligand of niobium (1.696(5) Å).[5b] Notably, the N···N distance of 2.56 Å is significantly outside the sum of the van deer Waals radii for two nitrogen atoms, indicating the complete cleavage of the former nitrogen triple bond.

Based on the chemical identity of complex **2** we speculated the identity of the lower yielding purple crystals to be that of either a radical anion or dianion possessing a similar diamond core structure. An X-ray diffraction study performed on a single purple crystal harvested from the reaction mixture confirmed the identity of this nitride to be the radical anion dimer $K[(ArO)_2Nb(\mu\text{-}N)]_2$ (**3**), a complex which retains the nearly symmetric diamond core structure with bridging Nb–N distances ranging 1.880(4)–1.910(4) Å (Fig. 1, Scheme 1). The K^+ interacts with one nitride ligand, and is partially encapsulated by three phenyl groups and an oxygen of one aryloxide ligand. Overall, complex **3** mirrors Cloke's nitride dimer $[K][V(N\{N'\}_2)(\mu\text{-}N)]_2$ ($[N\{N'\}_2]^{2-} = [(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2]$),[4a] if one ignores the weak amine interactions with the two vanadium centers. The anionic component also resembles Gambarotta's complex $[\{(Me_3P)_3V\}_2(\mu\text{-}H)_3][V(N\{SiMe_3\}_2)_2(\mu\text{-}N)]_2$.[7b] Although the diamond core structure of **3** deviates little from neutral **2**, solution magnetic measurements and an isotropic X-band EPR spectrum recorded on a toluene solution of **3** at room temperature validated the presence of a delocalized unpaired electron about the Nb_2N_2 core.† Complex **3** can be quantitatively converted to **2** *via* one-electron oxidation performed using AgOTf. Additionally, the conversion of **2** to **3** is accomplished in good yield (82% isolated) upon one-electron reduction using KC_8.

We have subsequently investigated the ability of complexes **2** and **3** to be surrogates for ammonia production derived from molecular nitrogen. Treatment of yellow **2** or purple **3**, dissolved in toluene, with anhydrous $HCl(Et_2O)$ (100 equivalents) results in a rapid color change to an orange-red solution. After allowing the reaction to proceed for 1 hour, all volatiles were removed and the resulting solids were analysed *via* ^{1}H NMR spectroscopy. Spectra recorded in DMSO-d_6 display a well-resolved equal intensity triplet ($^{1}J_{NH}$ = 50.5 Hz) centered at 7.49 ppm indicating NH_4Cl production. The HOAr ligand is clearly present in the ^{1}H NMR spectrum and exists in 2 : 1 ratio when compared to the integration of NH_4Cl. Production of ammonium chloride and HOAr were present in similar ratios for both complexes **2** and **3** and unequivocally demonstrate that these species contain a nitride derived from the only source of nitrogen available, N_2.

Intrigued by the numerous color changes upon reduction of dark-red **1** with *ca.* 6 equivalents of KC_8, we set out to isolate possible intermediates *enroute* to activation and splitting of N_2. Reduction of **1** using two equivalents of KC_8, performed in THF, results in formation of the yellow mononuclear Nb(IV) complex, [*trans*-$(ArO)_2NbCl_2(THF)_2$] (**4**) in 57% yield, whose identity was confirmed by solid state X-ray diffraction studies in addition to X-band EPR and solution magnetic measurements (Scheme 1).† Reduction and coordination of THF results in the formation of a discrete monomer, having the chlorides, THF and aryloxide ligands mutually *trans* to each other, forming a nearly perfect octahedral geometry.† We subsequently investigated the reduction of **1** with two additional electrons, using 4 equivalents of KC_8 in total. Addition of KC_8 to a dark-red toluene solution of **1** resulted in a gradual color change to yellow which slowly converges to a persistent green colored solution upon the final addition of KC_8. Following filtration, green crystalline material can be isolated which displays sharp resonances in the normal diamagnetic range of the ^{1}H and ^{13}C NMR spectra recorded in C_6D_6. Interestingly, the ^{1}H NMR spectrum displays four unique *tert*-butyl resonances suggesting an asymmetric molecule.† Green single crystals, grown from allowing a concentrated toluene solution layered with pentane to stand at room temperature for 5 hours, were subjected to an X-ray diffraction experiment revealing a dimeric structure of the chemical formula $K_3[(ArO)_4Nb_2(\mu\text{-}Cl)_3Cl_2]$ (**5**) (Fig. 2, Scheme 1). Surprisingly only a single equivalent of KCl has been eliminated, while the other three equivalents appear to play an important role in the stabilization of a dinuclear Nb(III)–ate complex. Each K^+ benefits from several interactions with chloride and aryloxide ligands at both the oxygen and aryl residues. The C_1 symmetry present in the solid-state structure of **5** is retained in solution and aids in explaining the four unique –OAr ligand

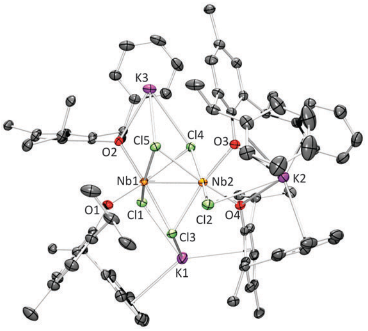

Fig. 2 Molecular structure of **5** with thermal ellipsoids at the 50% probability level. Carbons of the $-^tBu$ and $-CHPh_2$ groups as well as hydrogens have been omitted for clarity.

environments observed in the ^{1}H NMR spectrum. Noteworthy features of the solid-state structure are the short Nb–Nb distance (2.673 Å) and the face-sharing octahedral geometry of each niobium. Together these features suggest a significant degree of metal–metal interaction.[14] Complex **4** allows access to the nitride complexes **2** and **3** in similar yields upon reduction using the appropriate equivalents of KC_8 (Scheme 1). However, complex **5** only sluggishly converts to **2** in very low yields when subjected to similar reducing conditions suggesting that the strong Nb═Nb bond and bridging chlorides might hamper reactivity.

In conclusion, we have shown that entry to the niobium nitride functionality from N_2 activation and splitting can be readily accomplished using Nb(IV) and (V) complexes supported by the bulky and highly arylated aryloxide ligand. The system we described here somewhat mirrors Cloke's tridentate ligand scaffold $[N\{N'\}_2]^{2-}$ supporting vanadium.[4] However, our facile entry to these highly arylated aryloxide ligands allows us to prepare these precursors in bulk and to examine some of the intermediates formed in the activation and splitting of elemental nitrogen. Whether a Nb(II) fragment "$(ArO)_2Nb$" is generated in the course of these reactions is questionable since the K^+ counter cations seem to play a stabilization role in formation of "ate" complexes having low-valent Nb centers. Our work suggests that a dinuclear Nb(III) does not appear to activate N_2 and that bridging chlorides or strong Nb═Nb bond somewhat obstructs its reactivity with nitrogen. Current efforts are being placed in isolating such species as well as converting the nitride to more value-added ligands or fragments. Given the ease in preparing starting materials, in addition to the relatively inexpensive nature of niobium halide precursors such as $NbCl_5$, considerable efforts will be focused on rendering this reaction catalytic.

We thank Dr Nakamaru-Ogiso for collecting EPR spectra and the National Science Foundation for support of this work (CHE-1152123).

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