Niobium Methylidyne

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Formation and Redox Interconversion of Niobium Methylidene and Methylidyne Complexes

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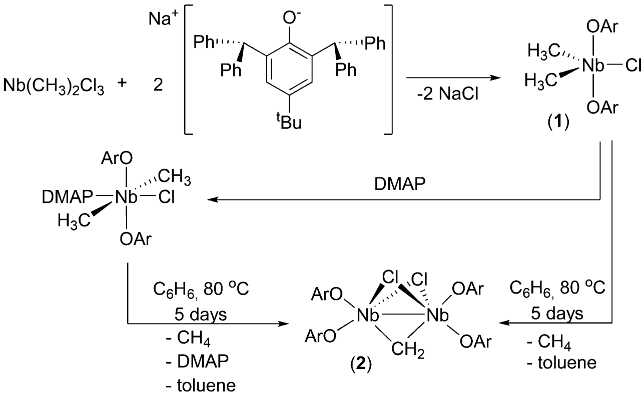
Abstract: *The niobium methylidene* $[\{(Ar'O)_2Nb\}_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}CH_2)]$ *(**2**) can be cleanly prepared via thermolysis or photolysis of* $[(Ar'O)_2Nb(CH_3)_2Cl]$ *(**1**) (OAr′ = 2,6-bis(diphenylmethyl)-4-tert-butylphenoxide). Reduction of **2** with two equivalents of* KC_8 *results in formation of the first niobium methylidyne* $[K][\{(Ar'O)_2Nb\}_2(\mu_2\text{-}CH)(\mu_2\text{-}H)(\mu_2\text{-}Cl)]$ *(**3**) via a binuclear α-hydrogen elimination. Oxidation of **3** with two equiv of* $ClCPh_3$ *reforms **2**. In addition to solid state X-ray analysis, all these complexes were elucidated via multinuclear NMR experiments and isotopic labelling studies, including a crossover experiment, support the notion for a radical mechanism as well as a binuclear α-hydrogen abstraction pathway being operative in the formation of **2** from **1**.*

Although methylidynes are known ligands for group 6 and 7 transition metals,[1,2] there are no reported methylidyne complexes with group 5 transition metals. This contrasts examples of substituted alkylidynes, where the hydrogen is replaced with a more sterically encumbering group.[3,4] Our group is particularly interested in this archetypal moiety since tantalum methylidenes and methylidynes, supported on a silicon oxide surface, have been implicated in the dehydrocoupling of methane to ethane and ethylene.[5] Therefore, we decided to explore niobium systems since this metal has more accessible low-valent states than tantalum and could allow us to probe redox processes involving the methylidyne ligand—such as α-elimination and α-migration. Herein, we report the synthesis and characterization of dinuclear complexes of niobium having bridging methylidene and methylidyne ligands. These dinuclear species are supported by the aryloxide ligand OAr″ (OAr′ = 2,6-bis(diphenylmethyl)-4-*tert*-butylphenoxide).[6] We propose the methylidene ligand to form via a radical mechanism pathway involving a $Nb_2^{IV,IV}$ dimer, combined with a binuclear α-hydrogen abstraction step. Formation of the first group 5 methylidyne complex occurs by a reductively promoted α-hydrogen elimination pathway involving two Nb^{III} centers. The methylidene and methylidyne moieties can interconvert via a two-electron redox process. Both of these species have been characterized in solution and by single crystal X-ray diffraction analysis (XRD).

On a multigram scale the precursor $[(Ar'O)_2Nb(CH_3)_2Cl]$ (**1**) (Scheme 1) can be readily prepared from the transmetallation of 2 equivalents of NaOAr″ with $[Nb(CH_3)_2Cl_3]$.[7] When treated with a strong Brønsted base such as the phosphorus ylide, H_2CPPh_3 (2 equivalents), a rare example of a terminally bound methylidene can be cleanly prepared, namely $[(Ar'O)_2Nb{=}CH_2(CH_3)(H_2CPPh_3)]$.[7] However, when complex **1** is thermalized at 80 °C, in the absence of a Brønsted base, a very slow reaction takes place over the duration of 5 days in benzene to cleanly form the bridging methylidene $[\{(Ar'O)_2Nb\}_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}CH_2)]$ (**2**) in 90 % isolated yield as a green-yellow product (Scheme 1). Formation of complex **2** can also be achieved via photoirradiation of complex **1** with a Xe lamp in benzene over a much shorter time period of 18 h. The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **2** indicate formation of a diamagnetic molecule where the methylidene ligand can be unambiguously identified. The methylidene resonance is unique in that it is the only CH_2^{2-} moiety in complex **2**. Hence, a DEPT-135 NMR experiment clearly identifies the methylidene carbon resonance at 172.48 ppm as the only negative peak in the DEPT trace of the spectrum. An HSQC NMR experiment correlates the former $^{13}C\{^1H\}$ NMR resonance to a ^1H NMR resonance at 5.78 ppm, integrating to two hydrogens. A solid-state single crystal structure of **2** further confirms the presence of two Nb^{IV} centers bridged by a methylidene ligand (Nb1–C145, 2.1194(16) Å; Nb2–C145, 2.1306(17) Å; Figure 1), where the hydrogens of the methylidene carbon



Scheme 1. Synthesis of the bridging methylidene complex **2** from thermolysis of **1** or **1**-DMAP.

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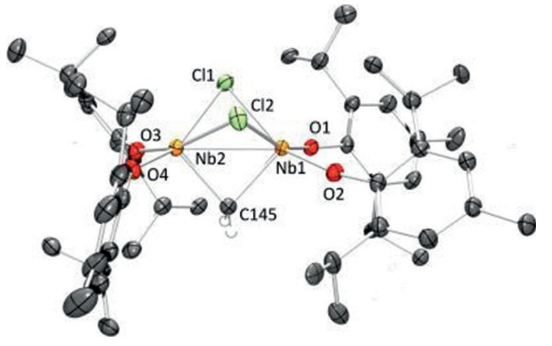
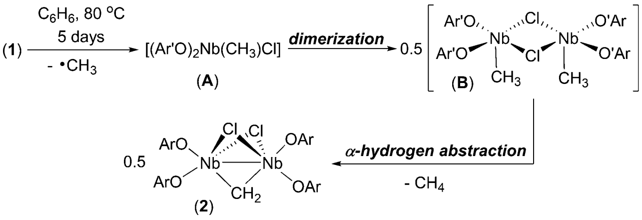


Figure 1. Molecular structure of complex **2** showing thermal ellipsoids at the 50% probability level. Carbons of the aryl $CHPh_2$ groups, ^{t}Bu groups, and hydrogen atoms (with the exception of the methylidene μ_2-CH_2) have been omitted for clarity.

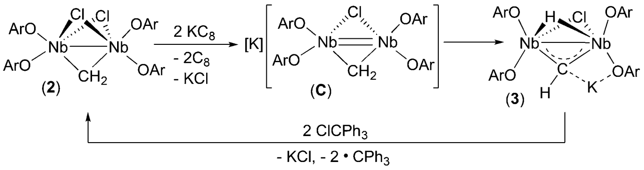
were located in the Fourier map and refined isotropically. In addition to a bridging methylidene, two chlorides are also shared between the two niobium centers. Each metal center retains two aryloxides resulting in a closed-shell species most likely having a Nb-Nb interaction (2.8329(2) Å). Although few examples of methylidenes exist for niobium,[7,8] the incorporation of a bridging methylidene from a Nb-methyl moiety has not been documented.

Monitoring the formation of **2** by thermolysis in C_6D_6 intermittently via ^{1}H NMR spectroscopy identifies only CH_4 and toluene-d_5 as by-products in the reaction mixture. The same products, in addition to detectable amounts of CH_3D, are formed when **1** is photoirradiated in C_6D_6 to produce **2**.[9] These observations suggest that **1** does not originate from the comproportionation of a Nb^{III} fragment $[(Ar'O)_2NbCl]$ with a four-coordinate Nb^{V} methylidene $[(Ar'O)_2Nb{=}CH_2(Cl)]$ since we fail to observe any formation of ethane. Instead our preferred proposed pathway for the formation of **2** involves a binuclear reaction where **1** undergoes Nb−C bond homolysis to form the intermediate $[(Ar'O)_2Nb(CH_3)Cl)]$ (**A**) and a methyl radical. The identification of trace amounts of toluene-d_5 in the reaction mixture is consistent with the formation of methyl radicals.[10] Subsequent dimerization of the Nb^{IV} fragments **A** would result in the intermediate $[\{(Ar'O)_2Nb(CH_3)\}_2(\mu_2\text{-}Cl)_2]$ (**B**), which would then undergo a binuclear α-hydrogen abstraction resulting in **2** along with methane (Scheme 2). Attempts to prevent dimerization or trap an intermediate in the reaction using a Lewis base such as 4-dimethylaminopyridine (DMAP) did not affect the outcome of the reaction since thermolysis of **1**-DMAP also yields **2** under identical conditions (Scheme 1). To further probe the mechanism to formation of **2** we prepared the isotopologue $[\{(Ar'O)_2Nb\}_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}CD_2)]$ (**2**-d_2) from the photolysis of $[(Ar'O)_2Nb(CD_3)_2Cl]$ (**1**-d_6, prepared from $[Nb(CH_3)_2Cl_3]$ and 2 equivalents of NaOAr′) in C_6D_6 and examined the organic products formed.[11] Not surprisingly, in C_6D_6, photolysis of **1**-d_6 produces the only isotope of methane, CD_4. More importantly, carrying out the reaction with a 50% mixture of **1** and **1**-d_6 in C_6D_6 revealed the formation of CH_4, CH_3D, CD_4 and CD_3H (confirmed from a combination of ^{1}H and ^{2}H NMR spectroscopy). The formation of CD_3H is only detected in the cross-over experiment and strongly supports a binuclear process involving an α-hydrogen abstraction. The crossover experiment resulted only in the formation of the isotopomers **2** and **2**-d_2, thus also consistent with a binuclear process taking place.



Scheme 2. Proposed mechanism to formation of **2**.

In attempts to explore the accessibility of low-valent states of niobium possessing a methylidene, the chemical reduction of complex **2** was investigated. When compound **2** was reduced with 2 equivalents of KC_8 in toluene, a new diamagnetic species was formed in 63% isolated yield as green crystals after removal of graphite and crystallization from a concentrated toluene solution layered with pentane (Scheme 3). The ^{1}H NMR spectrum of this new complex suggested formation of a highly asymmetric molecule with at least four different aryloxide environments when judged by the different *para*-^{t}Bu groups for each OAr′. The most intriguing feature of the ^{1}H NMR spectrum was a highly deshielded resonance at 13.18 ppm (1H), which was correlated to a highly deshielded ^{13}C NMR doublet resonance at 335.18 ppm ($^1J_{CH} = 150$ Hz) via an HSQC NMR experiment (Figure 2, left). It should be noted that the methylidyne ^{13}C NMR resonance could be directly detected in relatively short collection times via use of a DCH CryoProbe. The HSQC NMR spectrum also revealed a fairly broad resonance in the ^{1}H NMR spectrum at 5.07 ppm (1H) which did not correlate to any carbon resonances (Figure 2, right). These spectroscopic features suggest the formation of a dinuclear Nb complex having both a methylidyne and hydride ligand.



Scheme 3. Synthesis of the niobium methylidyne **3** and oxidation back to **2**.

To conclusively establish the degree of aggregation and connectivity involving these reactive ligand types we performed an XRD study on a green single crystal. Shown in Figure 3 is the molecular structure of the first niobium methylidyne, namely the ate-complex $[K\{(Ar'O)_2Nb\}_2(\mu_2\text{-}CH)(\mu_2\text{-}H)(\mu_2\text{-}Cl)]$ (**3**). Complex **3** crystallizes in the highly symmetric cubic *I*23 space group where the 101 867.2(19) Å^3 volume of the unit cell is comprised of 24 dinuclear molecules. The most notable features are the short and asymmetric niobium-methylidyne bonds at 1.977(4) and

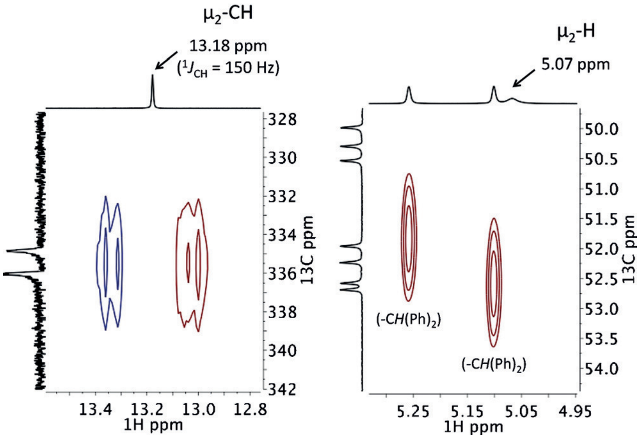


Figure 2. Expanded regions of the coupled (left) and decoupled (right) HSQC spectra of complex **3** showing the μ$_2$-CH (left) and μ$_2$-H (right) resonances.

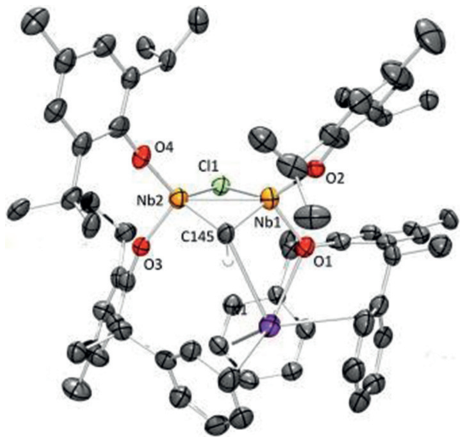


Figure 3. Molecular structure of complex **3** showing thermal ellipsoids at the 50% probability level. Carbons of the aryl CHPh$_2$ and ^{t}Bu groups, and hydrogen atoms (with the exception of the methylidyne μ$_2$-CH) have been omitted for clarity. The chloride is disordered over two positions and the hydride ligand could not be located from the XRD data.

2.018(4) Å. Further confirmation of the μ$_2$-CH ligand is the lone hydrogen located in the Fourier map for the methylidyne carbon. The methylidyne also interacts with a K$^+$ (C145–K1, 3.237(5) Å), which is further encapsulated by three aryl groups of the aryloxide ligands and one oxygen of an aryloxide ligand. The interactions of the aryl group with K$^+$ result in the aryloxide ligands being locked to render an overall C_1 symmetric complex having four different OAr′ environments. Based on our ^{1}H NMR spectroscopic data, the encapsulation of the K$^+$ is likely retained in solution at room temperature. Although each metal center is formally in a Nb^{IV} oxidation state for complex **3**, there is a significantly shorter Nb-Nb interaction (2.655(6) Å) when compared to complex **2**. Unfortunately, we were unable to locate a hydride in the Fourier map but our spectroscopic data clearly demonstrate complex **3** to have such a ligand, which we tentatively place as a bridging ligand.

The reduction of **2** to **3** implies that a transient Nb$_2^{III,III}$ methylidene, "[K][{(Ar′O)$_2$Nb}$_2$(μ$_2$-CH$_2$)(μ$_2$-Cl)] (**C**)", is likely being formed, and that a binuclear α-hydrogen elimination involving the methylidene C–H bond takes place to reoxidize each metal back to a Nb$_2^{IV,IV}$ core (Scheme 3). Notably, we can chemically promote migration of the hydride back to the methylidyne in **3** to reform **2** by addition of two equivalents of the oxidant ClCPh$_3$. This reaction resulted in formation of KCl along with one equivalent of Gomberg's dimer, the latter which we can observe by ^{1}H NMR spectroscopy (Scheme 3). Attempts to react **3** with only one equivalents of ClCPh$_3$ results in only 50% conversion to **2**. The formation of **2** from **3** mostly likely involves two one-electron oxidation steps and a hydrogen migration step (in no specific order).

In conclusion, we have reported a bridging methylidene complex of niobium via a Nb–CH$_3$ bond homolysis step followed by a binuclear α-hydrogen abstraction. Reduction of the Nb$_2^{IV,IV}$ core by two electrons resulted in α-hydrogen elimination to give rise to the first example of a group 5 methylidyne complex, which also contains a hydride ligand. Hydride migration back to the methylidyne can be readily accomplished by two electron oxidation. Isotopic labelling studies point towards a mechanism involving methyl radicals as well as a binuclear α-hydrogen abstraction process. We are now exploring the chemistry of these methylidyne with small molecules, in particular hydrocarbons since these species could model silicon oxide surfaces implicated in alkane C–H bond activation and dehydrocoupling reactions. Future work will also focus on the mechanism involving formation of **2** from **1**.

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[9] During the photoirradiation of **1** in C_6D_6 an impurity speculated to be $[(Ar'O)_2Nb(CH_3)Cl_2]$ was present. Given that photoirradiation produced CH_4 and CH_3D as the major and minor isotopes of methane, it is unclear if CH_3D is a direct product from the photoirradiation of **1**.

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[11] The complex $[(Ar'O)_2Nb(CD_3)_3]$ has been identified as a co-product in the ^{1}H NMR spectrum of the isotopolouge **1**-d_6. The protio derivative of this molecule has been independently synthesized and characterized. Photoirradiation of $[(Ar'O)_2Nb(CH_3)_3]$ has also been studied in C_6D_6 which produces CH_4 and CH_3D as the major and minor isotopes of methane. See Supporting Information for details.

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