A Terminally Bound Niobium Methylidyne

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Ⓢ *Supporting Information*

ABSTRACT: Complex (PNP)Nb(CH$_3$)$_2$(OAr) (PNP = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2$$^-$, Ar = 2,6-^{i}Pr$_2C_6H_3$), prepared from treatment of (PNP)NbCl$_3$ with NaOAr followed by 2 equiv of H$_3$CMgCl, can be oxidized with [FeCp$_2$][OTf] to afford (PNP)Nb(CH$_3$)$_2$(OAr)(OTf). While photolysis of the latter resulted in formation of a rare example of a niobium methylidene, (PNP)Nb=CH$_2$(OAr)(OTf), treatment of the dimethyl triflate precursor with the ylide H$_2$CPPh$_3$ produced the mononuclear group 5 methylidyne complex, (PNP)Nb≡CH(OAr). Adding a Brønsted base to (PNP)Nb=CH$_2$(OAr)(OTf) also resulted in formation of the methylidyne. Solid-state structural analysis confirms both methylidene and methylidyne moieties to be terminal, having very short Nb−C distances of 1.963(2) and 1.820(2) Å, respectively. It is also shown that methylidyne for nitride cross-metathesis between (PNP)Nb≡CH(OAr) and NCR (R = *tert*-butyl or 1-adamantyl) results in formation of a neutral and mononuclear niobium nitride, (PNP)Nb≡N(OAr), along with the terminal alkyne HC≡CR.

T he terminally bound methylidyne or parent carbyne, L$_n$M≡CH, is a rare ligand class prominent among group 6 transition metals.[1−6] High-oxidation-state transition metal methylidynes (d^0 metals) are even more scant, essentially constricted to several compounds: [N$_3$N]W≡CH (N$_3$N$^{3−}$ = [RNCH$_2$CH$_2$]$_3$N, R = Me$_3$Si, Me$_2$PhSi, MePh$_2$Si or C$_6$F$_5$),[7] ([Me$_3$SiNCH$_2$CH$_2$]$_3$N)Mo≡CH,[8] L$_n$W≡CH(H)(Cl)(X) (L$_n$ = two (H$_3$C)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$, or four P(CH$_3$)$_3$; X$^−$ = OTf or Cl),[9] (^{t}BuO)$_3$W≡CH(quin),[10] (^{t}Bu$_3$SiO)$_3$W≡CH,[11] and (Ar′[^{t}Bu]N)$_3$Mo≡CH (Ar′ = 3,5-Me$_2$C$_6$H$_3$).[12,13] Not surprisingly, cases of group 5 or earlier transition metal complexes having a terminal methylidyne are unknown. We specifically turned our attention to group 5 methylidynes, given the proposed role of high valent tantalum methylidynes, supported on silicon oxide surfaces, in methane activation and its dehydrocoupling to ethane and ethylene.[14] In such studies the role of the Ta−C multiple bond has been speculated to be critical in C−H bond activation and C−C coupling steps.[15] Of the group 5 transition metals we selected niobium because of its versatile 4+/5+ redox couple, therefore allowing us access to high-valent metal−ligand multiple bonds by virtue of an oxidatively induced α-hydrogen abstraction.[16] In this work we present a one-electron oxidation route to a niobium methylidene, which serves as a precursor to the first group 5 transition metal complex having a terminal methylidyne ligand. Synthesis and spectroscopic characterization, including structural information and methyl-

idyne group-transfer are presented for such a species. We also report the first neutral and mononuclear niobium nitride complex formed by a cross-metathesis reaction, as well as showcase some precursors or intermediates en route to formation of the Nb≡CH linkage.

Using the Nb(IV) precursor (PNP)NbCl$_3$ (PNP = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2$$^-$),[17] we first protected the metal center with the aryloxide $^-$OAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) via a salt elimination reaction to form (PNP)NbCl$_2$(OAr) (**1**) in 92% yield (Scheme 1). Complex **1** shows characteristic features typical for a d^1

Scheme 1. Synthesis of Complexes 1 and 2^a
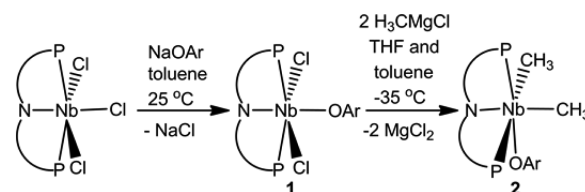
^{a}The ligands PNP and aryl group of the alkoxide have been simplified for clarity, where PNP = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2$$^-$ and Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

species (μ_{eff} = 1.83 μ_B), while single-crystal X-ray diffraction (XRD) analysis confirms this species to be a monomer having a Nb center in a nearly perfect octahedral geometry whereby the chlorides occupy trans positions.[18] Transmetalation of green **1** with 2 equiv of H$_3$CMgCl cleanly produces a dark-red solution from which the dimethyl complex (PNP)Nb(CH$_3$)$_2$(OAr) (**2**) is isolated in 75% yield (Scheme 1).

Akin to **1**, compound **2** displays similar spectroscopic and magnetic features. However, an XRD analysis reveals significant reorganization of the ligands, with the methyl ligands now oriented cis, therefore placing the aryloxide transoid to one of the pendant phosphines in the PNP ligand (Figure 1). Surprisingly, the geometrically constrained PNP scaffold now adopts a rare pseudo-facial configuration, while the Nb−C distances of 2.195(2) and 2.271(2) Å are typical for other reported Nb(IV) alkyls.[19] Our strategy in using the aryloxide in **2** is three-fold: We want to promote α-hydrogen abstraction of a methyl group, provide steric protection to the Nb−C multiple bond, and disfavor other side reactions such as α-elimination, which could lead to bis-methylidene products.[17] Such species have been shown to be thermodynamically favored when compared to their tautomeric alkylidyne-alkyl isomer, (PNP)M≡CR(CH$_2$R) (M = Nb,[17b] R = C(CH$_3$)$_3$ or Si(CH$_3$)$_3$; M = Ta, R = H).[20]
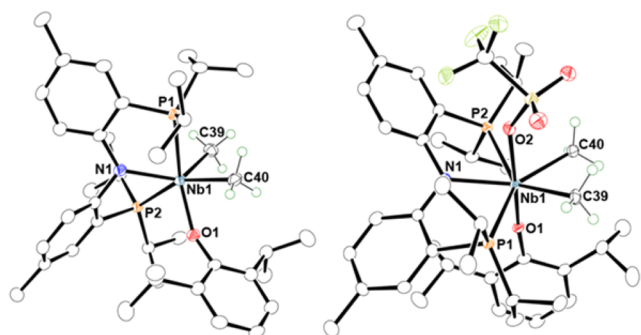
Figure 1. Molecular structures of **2** (left) and **3** (right), displaying thermal ellipsoids at the 35% probability level. Solvent and H-atoms, with the exception of α-hydrogens, have been omitted for clarity.

As expected for Nb(IV), complex **2** is a mild reductant, showing a reversible anodic wave at −1.01 V (versus FeCp$_2^{0/+}$).[18] At least three irreversible cathodic waves are observed for **2** above −2.34 V. Chemical oxidation of **2** with [FeCp$_2$][OTf] results in conversion to the Nb(V) species (PNP)Nb(CH$_3$)$_2$(OAr)(OTf) (**3**) in 70% isolated yield (Scheme 2). Complex **3** can be isolated

Scheme 2. Synthesis of Complexes 3−6[a]
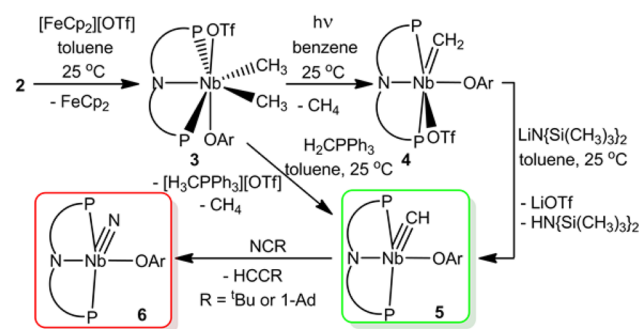
[a] The ligands PNP and aryl group of the alkoxide have been simplified for clarity, where PNP = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$ and Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

cleanly via sublimation of the FeCp$_2$ side product at 50−60 °C under dynamic vacuum (ca. 0.1−0.2 mmHg). Other one-electron oxidants such as AgOTf, ClCPh$_3$, and TEMPO, when combined with **2**, resulted in complicated mixtures, some of which included oxidation of the Nb−C bond to form Nb(IV) species. As anticipated for a coordinatively saturated Nb complex, the ^{1}H NMR spectral analysis of **3** is consistent with an averaged C_1 symmetric system having broadened and inequivalent methyl groups. Likewise, the ^{31}P NMR spectrum reveals two broad resonances at 38.9 and 50.3 ppm. XRD structural analysis of **3** confirms the formation of a pentagonal-bipyramidal d^0 species having cis-oriented dimethyl ligands in nearby proximity (C−Nb−C, 71.95(12)°), whereby both triflate and aryloxide are transoid (Figure 1). Despite **3** being high-valent, its higher coordination geometry results in significantly elongated Nb−C distances (2.287(3) and 2.302(3) Å) when compared to **2**.

Although complex **3** can be isolated in good yield, this species is light-sensitive. Exposure of **3** to a Xe lamp with UV mirror module (250−385 nm) results in a color change from dark red to dark yellow. Examination of the volatiles reveals methane to be the only product formed (by ^{1}H NMR spectroscopy), and

workup of the residue results in isolation of a new diamagnetic material in 77% yield.

The ^{1}H NMR spectrum shows two broad resonances at 11.4 and 12.2 ppm, each integrating to one hydrogen. All other spectroscopic features in the ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectrum are consistent with such a species being C_1-symmetric, in accord with formation of the complex (PNP)Nb═CH$_2$(OAr)(OTf) (**4**) (Scheme 2). Unfortunately, we were unable to observe the methylidene resonance in the ^{13}C NMR spectrum presumably due to coupling of it to the ^{93}Nb quadrupolar nucleus ($I = 9/2$, 100%). For this reason we prepared the isotopologue (PNP)Nb═^{13}CH$_2$(OAr)(OTf) (**4-^{13}C**)[18] and observed a highly downfield broadened resonance at 282 ppm in the ^{13}C NMR spectrum, which in turn could be correlated to the two downfielded resonances in the ^{1}H NMR spectrum via an ^{1}H−^{13}C HMQC experiment ($^1J_{CH}$ = 129 and 134 Hz). Few examples of terminally bound niobium methylidenes exist,[21,22] and complex **4** represents a rare case where the methylidene ligand could be further deprotonated, given the presence of a $^-$OTf leaving group. An XRD study of **4** (Figure 2) indeed
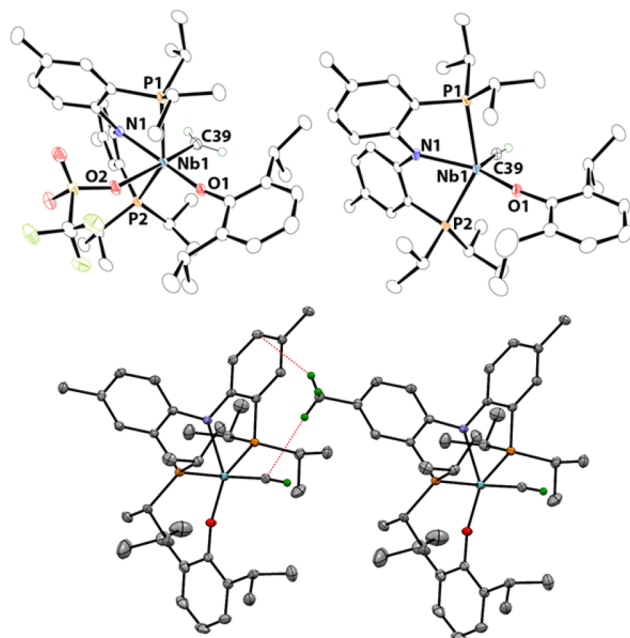

Figure 2. Molecular structures of **4** (top left) and **5** (top right), showing thermal ellipsoids at the 35% probability level. Solvent and H-atoms, with the exception of α-hydrogens, have been omitted for clarity. Below is an expansion of the packing diagram, showing the interaction of the methylidyne carbon with the tolyl hydrogens of the PNP ligand.

confirms the presence of a terminal methylidene group with a comparable Nb═C distance (1.962(2) Å) to the only other structurally characterized example, (Ar′O)$_2$Nb═CH$_2$(CH$_3$)(H$_2$CPPh$_3$) (1.9411(16) Å).[22] Complex **4** adopts a pseudo-octahedral geometry, with the methylidene ligand being oriented trans to $^-$OTf. The hydrogen atoms on the methylidene carbon where located and refined isotropically, therefore revealing the π-bond to be oriented along the P−Nb−P vector. This orientation is intuitively expected on the basis of orbital arguments, given the π-donor ligands (arylamide and aryloxide) residing along the plane defined by the atoms NbNO$_2$C. If one ignores the more labile $^-$OTf, the geometry of the fragment [(PNP)Nb═CH$_2$(OAr)]$^+$ is akin to the square-pyramidal and isovalent methylidene complex

$(PNP)Zr=CH_2(OAr)$.[23] The orientation of the methylidene hydrogens also explains why these are symmetrically inequivalent based on the ^{1}H NMR spectrum

Whereas terminal methylidynes for complexes of Mo,[8,12] W,[1−7,9−11] and Os[24] are known, terminally bound methylidynes for group 5 transition metals are not.[25] To date, only a few examples of bridging alkylidyne complexes of Nb exist,[26] while a handful of substituted alkylidyne bound terminally to vanadium and tantalum have been reported.[27] Having 3 in hand, we treated it with H_2CPPh_3 in toluene at room temperature to rapidly form a new green-colored metal species quantitatively, along with precipitation of the salt $[H_3CPPh_3][OTf]$. Examination of the volatiles revealed CH_4 as a side-product and subsequent workup and crystallization of the residue from pentane exposed a broad resonance at 6.0 ppm in the ^{1}H NMR spectrum, which integrated to one hydrogen. Since d^0 methylidyne complexes are exceptionally rare, we explored the solid-state structure via an XRD study. Figure 2 displays the first monomeric and square-pyramidal Nb(V) methylidyne complex $(PNP)Nb\equiv CH(OAr)$ (5) ($\tau_5 = 0.03$),[28] possessing the shortest $Nb\equiv C$ bond length known to date (1.820(2) Å). Notably, the methylidyne H was located from the difference map, but not refined isotropically since it yielded an unrealistically short C−H bond distance of 0.83(3) Å.[29] Another salient feature in the solid-state structure of 5 is evident from the examination of the packing diagram. The bottom of Figure 2 portrays a component of the packing structure of 5 emphasizing a long but notable interaction between the methylidyne carbon and tolyl methyl group of the PNP in a neighboring molecule (2.87 Å). This interaction most likely explains why the $Nb\equiv CH$ angle (172.9°, not refined) is slightly distorted from linearity. Such a phenomenon was similarly observed by Hopkins and co-workers in the d^2 compound $(dmpe)_2W=CH(^nBu)$ (~2.84 Å).[3b] The gross geometry in complex 5 also mirrors $(PNP)Zr=CH_2(OAr)$,[23] recently reported by our group. Formation of 5 from 3 most likely traverses via an intermediate such as 4, and independent studies do confirm that addition of a Brønsted base ($LiN\{Si-(CH_3)_3\}_2$ or H_3CMgCl) to 4 rapidly yields the methylidyne without any spectroscopic evidence for the transmetalated species "$(PNP)Nb=CH_2(OAr)(X)$" (X = $N\{SiMe_3\}_2$ or CH_3). Whereas the amide cleanly produces 5 from 3, the use of methyl Grignard leads to some reduction products which we have been unable to characterize.[18] To spectroscopically confirm formation of a terminally bound methylidyne moiety, we prepared the isotopologue $(PNP)Nb\equiv^{13}CH(OAr)$ (5-^{13}C) from precursor 3-[13]C.[18] Figure 3 clearly shows how the ^{1}H NMR spectroscopic resonance at 6.0 ppm is correlated to a highly downfield ^{13}C NMR resonance at 294 ppm via an HMQC experiment and with a $^1J_{CH}$ value of 134 Hz (inset of Figure 3).

Having a highly nucleophilic methylidyne 5 in hand, we explored "CH" group transfer in hopes of making a neutral and terminally bond niobium nitride. Accordingly, we looked into a methylidyne for a nitride cross-metathesis reaction using the nitrile NC^tBu. Upon addition of the nitrile to 5, a color change from green to red-brown occurred, and monitoring of the reaction mixture revealed formation of an intermediate (^{31}P NMR: 42.7 and 53.4 ppm), which gradually changed to a new species having ^{31}P NMR resonances at 37.1 and 43.1 ppm. Workup of the reaction mixture resulted in the formation of $HC\equiv C^tBu$ along with a new inorganic complex we propose to be $(PNP)Nb\equiv N(OAr)$ (6) on the basis of ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data (Scheme 2). Overall, NMR spectroscopic data of 6 are similar to 5 (but lacking the methylidyne
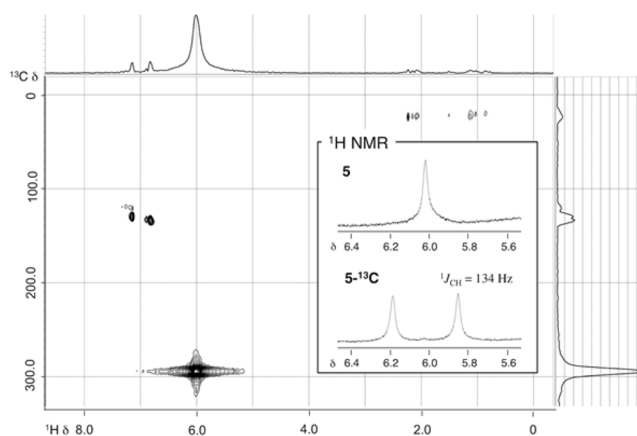

Figure 3. Expanded $^1H-^{13}C$ HMQC spectrum for complex 5-^{13}C, with inset showing an expanded ^{1}H NMR spectrum for 5 (top) and 5-[13]C (bottom).

resonance). Using the 40% ^{15}N-enriched nitrile $^{15}NC[1-Ad]$ (1-Ad = 1-adamantyl)[30] with 5, we observed quantitative conversion to the ^{15}N enriched isotopomer $(PNP)Nb\equiv^{15}N(OAr)$ (6-^{15}N) concurrent with HCC[1-Ad] (Scheme 2). Likewise, treating 5-^{13}C with $^{15}NC[1-Ad]$ also resulted in formation of 6-^{15}N along with $H^{13}CC[1-Ad]$, which was unambiguously confirmed via ^{13}C NMR spectroscopy (67.6 ppm).[18] The ^{15}N NMR spectrum of 6-^{15}N corroborates the formation of a terminally bound niobium nitride given the highly deshielded resonance at 833 ppm ($\Delta\nu_{1/2}$ = 10 Hz, referenced to $^{15}NC[1-Ad]$ at 242 ppm).[18,31] Despite not having single-crystal XRD data for 6, the ^{15}N NMR spectroscopic data suggest this species to be a monomer and to have a geometry very similar to that of 5. Formation of 6 and HCCR from 5 and NCR (R = ^tBu or 1-Ad) mostly likely traverses through an azametallacyclobutadiene $[(PNP)Nb(NCRCH)(OAr)]$ (A),[30,32] which then [2+2] retro-cyclo-eliminates the terminal alkyne with formation of the metal nitride ligand (Scheme 3).

Scheme 3. Proposed Mechanism in the Formation of 6 from 5 and Nitrile NCR[a]
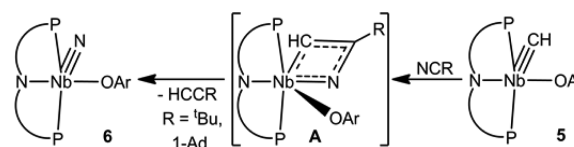
[a]The ligands PNP and aryl group of the alkoxide have been simplified for clarity, where PNP = $N[2-P^iPr_2-4-methylphenyl]_2^-$ and Ar = $2,6-^iPr_2C_6H_3$).

In conclusion, we show that the first methylidyne of a group 5 metal can be prepared via an α-hydrogen abstraction step and Brønsted base-induced HOTf elimination. Although α-hydrogen abstraction is a common approach to Schrock-like alkylidene and alkylidynes, the key step to retain both methyls and a leaving group such as ^-OTf is the one-electron oxidation reaction from Nb(IV) to Nb(V). Alkylation in a lower oxidation state results in minimal redox side reactions, whereas the oxidation step readily integrates a ^-OTf leaving group in the high-valent state. The methylidyne ligand can undergo cross-metathesis with a nitrile to afford the first example of a neutral and terminally bound niobium nitride. Other reactivity of the niobium methylidyne and its isovalent nitride species will be forthcoming.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00830.

Crystallographic data and tables, experimental details, and NMR spectral data (PDF)

X-ray crystallographic data for **1−5** (CIF)

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Notes

The authors declare no competing financial interest.

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