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COMMUNICATION

Binary Role of an Ylide in Formation of a Terminal Methylidene Complex of Niobium

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The first structurally characterized niobium(V) complex possessing a terminal methylidene ligand is reported in high yield from the reaction of [(Ar'O)₂Nb(CH₃)₂Cl] (Ar' = (2,6-CHPh₂)₂-4-*t*Bu-C₆H₂) and two equivalents of H₂CPPPh₃.

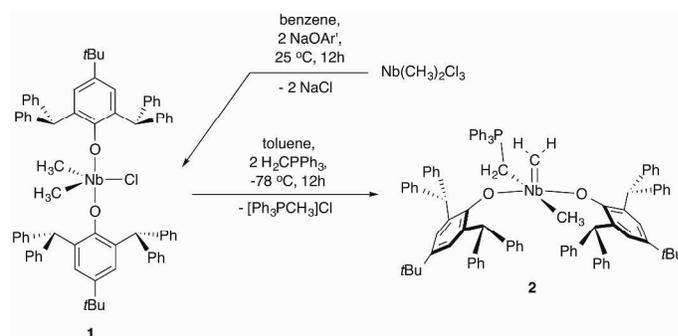
Since the initial discovery of [Cp₂Ta=CH₂(CH₃)] by Schrock and Sharp,¹ terminal methylidene complexes have emerged as key ligands in many important transformations such as olefination/homologation and group transfer catalysis.²⁻⁶ These intriguing molecules are also thought to be relevant for technical applications such as the Fischer-Tropsch process,⁷⁻⁹ which has gained renewed prominence as a possible solution to the impending energy crisis. Additionally, terminal transition metal methylidenes are reactive intermediates in C-X and other bond activation pathways^{6,10-13} as well as C=C bond forming processes that ultimately result in deactivation of olefin metathesis catalysis.^{1,14} More recently, tantalum methylidenes and methylidyne complexes attached to a silicon oxide surface were proposed to formally accomplish alkane metathesis resulting in the conversion of methane to ethane and even ethylene.¹⁵ Whereas tantalum methylidene complexes can now be considered known,^{1,6,10,16} studies on analogous niobium methylidenes are exceedingly rare, possibly due to the propensity of Nb^V to form Nb^{IV} and/or Nb^{III} species.¹ Some of these few examples may be accessed via oxidation of reactive Nb^{III} precursors,¹² trapped,¹⁷ or produced in an argon matrix by laser-ablation when exposed to a suitable CH₂ source such as methane or FCH₃.¹⁸ Inspired by work of Rothwell,¹⁰ we report herein that a terminal niobium methylidene complex can be prepared in a convenient manner by using the ylide H₂CPPPh₃ as a base and a ligand trap. The target complex was fully characterized and theoretical studies were conducted to better understand the electronic structure of the novel niobium methylidene complex. Some preliminary reactivity involving the Nb=CH₂ ligand is also presented.

We recently reported the synthesis of a sterically encumbering aryloxy ligand, ⁻OAr' (Ar' = (2,6-CHPh₂)₂-4-*t*Bu-C₆H₂), designed to be impervious to cyclometallation chemistry, often observed with other more common and sterically demanding alkoxide ligands such as ⁻OAr (Ar = (2,6-*i*Pr₂)C₆H₃, (2,6-Ph₂)C₆H₃, or (2,6-*t*Bu₂)-4-R-C₆H₂ where R = H, Me or *t*Bu), given the unlikely formation of a seven membered metallacycle involving the 2,6-diphenylmethyl

substituents. We have reported this ancillary ligand to be compatible with a variety of early 3d transition metals.¹⁹ The ligand is so sterically demanding that only two aryloxides can be bound to a metal ion, despite using forcing conditions.

The methylidene precursor was prepared by treating the dimethyl complex [Nb(CH₃)₂Cl₃]²⁰ with two equivalents of NaOAr' in benzene. After stirring the reaction mixture for 12 hours, workup of the resulting yellow-brown solution afforded a yellow solid in 72% isolated yield, which was characterized as [(Ar'O)₂Nb(CH₃)₂Cl] (**1**) (Scheme 1). The molecule exhibits C_{2v} symmetry based on its ¹H NMR spectrum and the solid-state X-ray structure shows this species to have almost perfect bipyramidal geometry (τ = 0.96).²¹ The solid-state structure determination of

Scheme 1. Synthesis of complexes **1** and **2**.



compound **1**[†] is similar to that of a niobium analogue reported by Rothwell, namely the complex [(ArO)₂Nb(CH₂Ph)₂Cl] (Ar = (2,3,5,6-Ph₄)C₆H),²² where the two alkoxides are positioned in an eclipsed orientation to each other.

Treatment of **1** with one equivalent of the base H₂CPPPh₃²³ led to formation of a new product along with unreacted material. Addition of two equivalents of the Wittig reagent improved the isolated yield of the new complex, [(Ar'O)₂Nb=CH₂(CH₃)(H₂CPPPh₃)] (**2**), to 87%. We chose a Wittig reagent as the base due to the ease of separating the salt [H₃CPPPh₃][Cl]. The same strategy was originally used by

Schrock and Sharp to prepare $[(\text{Cp})_2\text{Ta}=\text{CH}_2(\text{CH}_3)]^1$ from the deprotonation of $[(\text{Cp})_2\text{Ta}(\text{CH}_3)_2][\text{BF}_4]$ and was later employed by Arnold^{16d} involving $[(\text{Me}_3\text{SiNCPPhNSiMe}_3)_2\text{Ta}(\text{CH}_3)_2(\text{OTf})]$ in the synthesis of an electronically unsaturated tantalum methylidene. The ^1H NMR spectrum of the new complex possesses an array of broad and overlapping multiplets spanning 8.00-6.20 ppm. A downfield doublet integrating to 2 protons is centered at 9.94 ppm ($^4J_{\text{HP}} = 1.4$ Hz) and is consistent with a methylidene fragment being formed and the complex having C_s symmetry in solution.¹² An HSQC experiment clearly shows correlation of the latter resonance in the ^1H NMR spectrum to an sp^2 ^{13}C NMR resonance at 230.7 ppm. In a multiplicity-edited HSQC NMR spectrum, the downfield resonance of 230.7 ppm reveals a $^1J_{\text{CH}}$ of 139 Hz (See ESI), typical of terminal methylidenes not engaged in agostic interactions with the metal center to any notable extent.^{1,12,16} Variable temperature ^1H NMR spectroscopic studies of **2**, collected between 25 and -55 °C in THF- d_8 , suggest that there is no rotation of the methylidene fragment as this resonance experiences no change. Hence, all our NMR spectroscopic data, in addition to combustion analysis support the formation of **2**. However, to conclusively establish that the methylidene ligand was terminal, we performed X-ray diffraction studies on a single crystal.

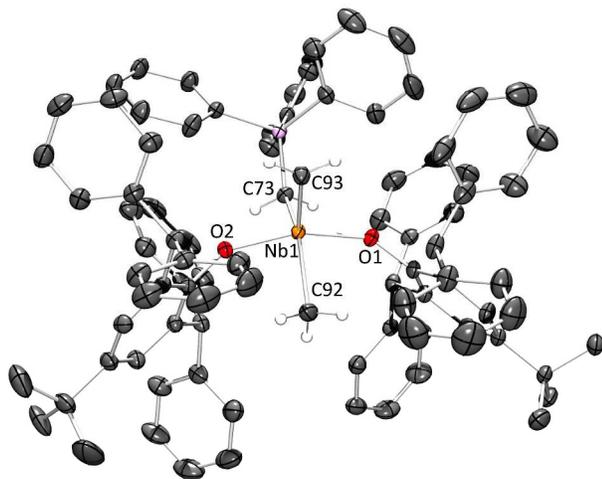


Figure 1. Molecular structure of $[(\text{Ar}'\text{O})_2\text{Nb}=\text{CH}_2(\text{CH}_3)(\text{H}_2\text{CPPh}_3)]$ (**2**) with thermal ellipsoids at the 50% probability level. Only α -hydrogens are shown for clarity.

Figure 1 displays the solid-state structure of **2**[†] revealing a Nb^V center in a distorted-square pyramidal geometry ($\tau = 0.33$).²¹ The basal plane of the structure is comprised of the methyl, H_2CPPh_3 and the transoid aryloxy ligands, rendering the terminal methylidene ligand axial. Perhaps the most notable feature is the Nb1-C93 distance of 1.9411(16) Å for the methylidene ligand, which is a remarkably shorter bond length than the Nb1-C73 distance of 2.3540(15) Å, seen for the Nb- CH_2 fragment of the bound ylide. It is also much shorter than the Nb-methyl distance of 2.2449(2) Å. The two hydrogen atoms on the methylidene carbon were located in the Fourier map and refined isotropically providing additional support for the assignment of a terminal methylidene. Orientation of the methylidene-hydrogens indicate that the Nb= CH_2 π -bond is formed in an orthogonal direction to the O-Nb-O axis and as a result of π -donation of the carbene into the empty d_{xz} orbital of niobium. The triphenylphosphine substituent of H_2CPPh_3 points toward the

methylidene, providing steric protection. The ylide protects the methylidene ligand and virtually behaves as a trap for the “[$(\text{Ar}'\text{O})_2\text{Nb}=\text{CH}_2(\text{CH}_3)$]” fragment akin to Rothwell’s reactive $[(\text{ArO})_2\text{Ta}=\text{CH}_2(\text{CH}_3)]$ ($\text{ArO}^- = (2,6\text{-}t\text{Bu}_2)\text{C}_6\text{H}_3$) system that is known to activate intramolecular C-H bonds of its aryloxy ligands.¹⁰ The bent geometry of both aryloxides ($145.78(10)$ and $147.26(10)^\circ$) can be attributed to steric repulsion of the ylide ligand and the need of unoccupied π^* orbitals for stabilization of the methylidene. To our knowledge, complex **2** marks the first example of a structurally characterized terminal niobium methylidene.

Complex **2** is stable when stored as a solid at -35 °C. However, at room temperature benzene solutions gradually decompose over 1 week with release of methane, which we were able to detect by ^1H NMR spectroscopy. Unfortunately, we were unable to trap the organometallic product that likely results from this transformation.

To understand the bonding and site of reactivity of **2** we performed DFT calculations. Our calculations reveal that the HOMO of **2** is comprised of π -donation of the methylidene p_x -orbital into the niobium d_{xz} orbital, which is anti-bonding with respect to the Nb- CH_3 bond (Figure 2). Population of this Nb- CH_3 σ^* -orbital results in a slight lengthening of the niobium-methyl bond ($2.252_{\text{calc}}/2.250_{\text{exp}}$ Å). To avoid the anti-bonding interaction with the out-of-phase lobe of Nb- d_{xz} , the methyl is angled such that the methyl- p_x can form what is essentially a three-center two-electron bond with the niobium and the methylidene. The Nb= CH_2 bond length ($1.941_{\text{calc}}/1.941_{\text{exp}}$ Å) is significantly shorter than the Nb- CH_3 bond length and the Mayer-Mulliken bond order for the former was calculated to be 1.729, compared to 0.916 for the Nb- CH_3 single bond. The lowest unoccupied metal based orbitals of **2** are d_{xy} and d_{yz} , which are located 3.764 and 4.079 eV higher in energy than the HOMO, respectively. This molecular orbital occupation pattern is fully consistent with a Nb^V-carbene complex and we categorize this complex as a Schrock-carbene, and thus expect that the methylidene should be nucleophilic.

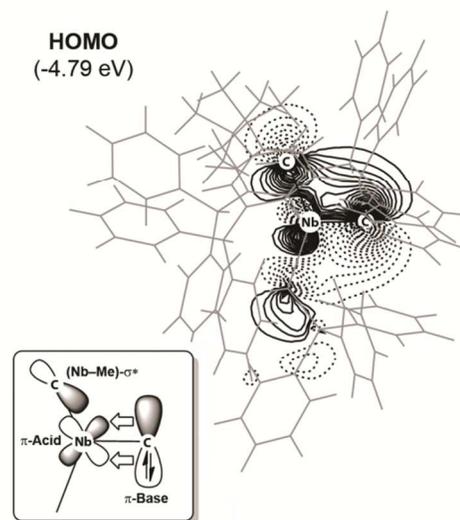
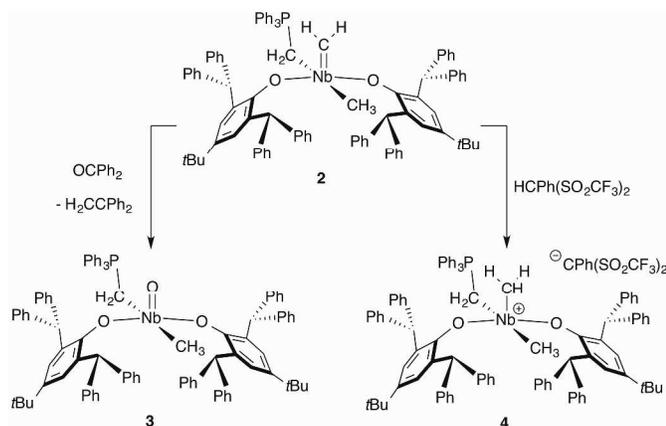


Figure 2. Contour plot showing iso-densities of the HOMO of **2**, reflecting the π -donation of the methylidene p_x -orbital into the niobium d_{xz} -orbital.

Scheme 2 displays some preliminary reactivity of **2** with electrophiles. Benzophenone rapidly reacts with the methylidene ligand in **2** to form the olefin $\text{H}_2\text{C}=\text{CPh}_2$ and niobium oxo $[(\text{Ar}'\text{O})_2\text{Nb}=\text{O}(\text{CH}_3)(\text{H}_2\text{CPPh}_3)]$ (**3**) in 79% isolated yield. The ^1H

and ^{13}C NMR spectra of **3** are quite similar to **2**, but in absence of the downfield methylidene resonances at 9.94 and 230.70 ppm, respectively. These results indicate that there is negligible structural change when the methylidene ligand is replaced with an oxo. X-ray diffraction studies performed on yellow single crystals of **3** confirm a distorted-square pyramidal geometry ($\tau = 0.29$)²¹ similar to **2**.[†] Exposure of **2** to the acid $\text{HCP}(\text{SO}_2\text{CF}_3)_2$ ²⁴ in toluene at room temperature results in rapid protonation of the methylidene ligand to form the dimethyl salt $[(\text{Ar}'\text{O})_2\text{Nb}(\text{CH}_3)_2(\text{H}_2\text{CPPh}_3)][\text{CPh}(\text{SO}_2\text{CF}_3)_2]$ (**4**). Complex **4** is a yellow solid which is sparingly soluble in aromatic solvents and gradually decomposes, thus preventing us from obtaining clean NMR spectroscopic data. However, yellow single crystals can be grown rapidly at low temperature and the solid-state structure confirms the methylidene as the site of protonation, whereby the Nb-C distance has elongated to 2.1222(18) Å and is comparable to the other methyl group (Nb1-C92, 2.1579(18) Å).[†] Overall, the gross geometry of $[(\text{Ar}'\text{O})_2\text{Nb}(\text{CH}_3)_2(\text{H}_2\text{CPPh}_3)]^+$ is similar to **2** again reiterating the rigidity of the ylide and aryloxy ligands, but also the nucleophilic site of the methylidene.

Scheme 2. Reactivity of the methylidene complex **2** with a ketone and a crystalline proton source to form an oxo **3** and dimethyl cation **4**, respectively.



We have prepared and characterized a rare example of a terminally bound niobium methylidene and examined some preliminary reactivity. Our approach to generating the methylidene group on niobium involves a straightforward protocol using one equivalent of ylide as ligand and the other as a Brønsted base.

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Notes and references

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[†]CCDC-980858 through 980861 contains the supplementary crystallographic data for this paper.

Electronic Supplementary Information (ESI) available: Compounds **1-4**. See DOI: 10.1039/c000000x/

- a) R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 6577; b) L. J. Guggenberger, and R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 6578; c) R. R. Schrock, and P. R. Sharp, *J. Am. Chem. Soc.*, 1978, **100**, 2389.
- J. Scott, and D. J. Mindiola, *Dalton Trans.*, 2009, 8463.
- N. A. Petasis, S.-P. Lu, E. I. Bzowje, D.-K. Fu, J. P. Staszewski, I. Akritopoulou-Zanze, M. A. Patane, and Y.-H. Hu, *Pure Appl. Chem.*, 1996, **68**, 667.
- F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611.
- T. R. Howard, J. B. Lee, and R. H. Grubbs, *J. Am. Chem. Soc.*, 1980, **102**, 6876.
- a) D. H. Berry, T. S. Koloski, and P. J. Carroll, *Organometallics* 1990, **9**, 2952; b) S. M. Mullins, R. G. Bergman, and J. Arnold, *Dalton Trans.*, 2006, 203; c) A. J. Jiang, J. H. Simpson, P. Müller, and R. R. Schrock, *J. Am. Chem. Soc.*, 2009, **131**, 7770; d) R. R. Schrock, A. J. Jiang, S. C. Marinescu, J. H. Simpson, and P. Müller, *Organometallics* 2010, **29**, 5241.
- L. E. McCandlish, *J. Catal.*, 1983, **83**, 362.
- E. L. Hoel, G. B. Ansell, and S. Leta, *Organometallics* 1984, **3**, 1633.
- G. Proulx, and R. G. Bergman, *Science* 1993, **259**, 661.
- a) I. P. Rothwell, *Acc. Chem. Res.*, 1988, **21**, 153; b) L. R. Chamberlain, I. P. Rothwell, and J. C. Huffman, *J. Am. Chem. Soc.* 1986, **108**, 1502; c) L. R. Chamberlain, A. P. Rothwell, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1984, **106**, 1847.
- C. McDade, J. C. Green, and J. E. Bercaw, *Organometallics*, 1982, **1**, 1629.
- K. F. Hirsekorn, A. S. Veige, and P. T. Wolczanski, *J. Am. Chem. Soc.*, 2006, **128**, 2192.
- D. P. Klein, and R. G. Bergman, *J. Am. Chem. Soc.*, 1989, **111**, 3079.
- S. Arndt, R. R. Schrock, and P. Müller, *Organometallics* 2007, **26**, 1279.
- D. Soulivong, S. Norsic, M. Taoufik, C. Coperet, J. Thivolle-Cazat, S. Chakka, and J.-M. Basset, *J. Am. Chem. Soc.*, 2008, **130**, 5044.
- a) A. van Asselt, B. J. Burger, V. C. Gibson, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1986, **108**, 5347; b) G. Parkin, E. Bunel, B. J. Burger, M. S. Trimmer, A. van Asselt, and J. E. Bercaw, *J. Mol. Catal.*, 1987, **41**, 21; c) D. M. Antonelli, W. P. Schaefer, G. Parkin, J. E. Bercaw, *J. Organomet. Chem.*, 1993, **462**, 213; d) D. Y. Dawson, and J. Arnold, *Organometallics* 1997, **16**, 1111; e) M. D. Fryzuk, Johnson, S. A.; and S. J. Rettig, *Organometallics* 1999, **18**, 4059; f) M. D. Fryzuk, S. A. Johnson, and S. J. Rettig, *J. Am. Chem. Soc.*, 2001, **123**, 1602; g) S. M. Mullins, R. G. Bergman, and J. Arnold, *Organometallics* 1999, **18**, 4465; h) S. M. Mullins, R. G. Bergman, and J. Arnold, *Dalton Trans.*, 2006, 203; i) L. C. H. Gerber, L. A. Watson, S. Parkin, W. Wang, B. M. Foxman, and O. V. Ozerov, *Organometallics* 2007, **26**, 4866.
- K. Mashima, M. Kaidzu, Y. Nakayama, and A. Nakamura, *Organometallics* 1997, **16**, 1345.
- a) H.-G. Cho, *J. Korean Chem. Soc.*, 2006, **50**, 415; b) H.-G. Cho, and L. Andrews, *Organometallics* 2006, **25**, 477.
- K. Searles, B. L. Tran, M. Pink, C. Chun-Hsing, and D. J. Mindiola, *Inorg. Chem.*, 2013, **52**, 11126.
- a) P. A. Belmonte, F. G. N. Cloke, K. H. Theopold, and R. R. Schrock, *Inorg. Chem.* 1984, **23**, 2365; b) We have found that $\text{Nb}(\text{CH}_3)_2\text{Cl}_3$ is sensitive to incandescent light which degrades the complex to an unidentified insoluble brown solid. Thus, the synthesis of $\text{Nb}(\text{CH}_3)_2\text{Cl}_3$ and complex **1** are performed in the absence of light.
- a) τ is defined as $(A-B)/60$, with A and B being the largest and smallest metal-ligand angles in the base of an approximate square pyramidal geometry, where $\tau = 0$ for square pyramidal and $\tau = 1$ for trigonal bipyramidal; b) A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn, and G. C. Verschoor, *Dalton Trans.*, 1984, 1349.
- S. W. Schweiger, M. M. Salberg, A. L. Pulvirenti, E. E. Freeman, P. E. Fanwick, and I. P. Rothwell, *Dalton Trans.*, 2001, 2020.
- H. J. Bestmann, W. Stransky, and O. Vostrowsky, *Chem. Ber.*, 1976, **109**, 1694.

24 J. Koshar, and R. A. Mitsch, *J. Org. Chem.*, 1973, **38**, 3358.