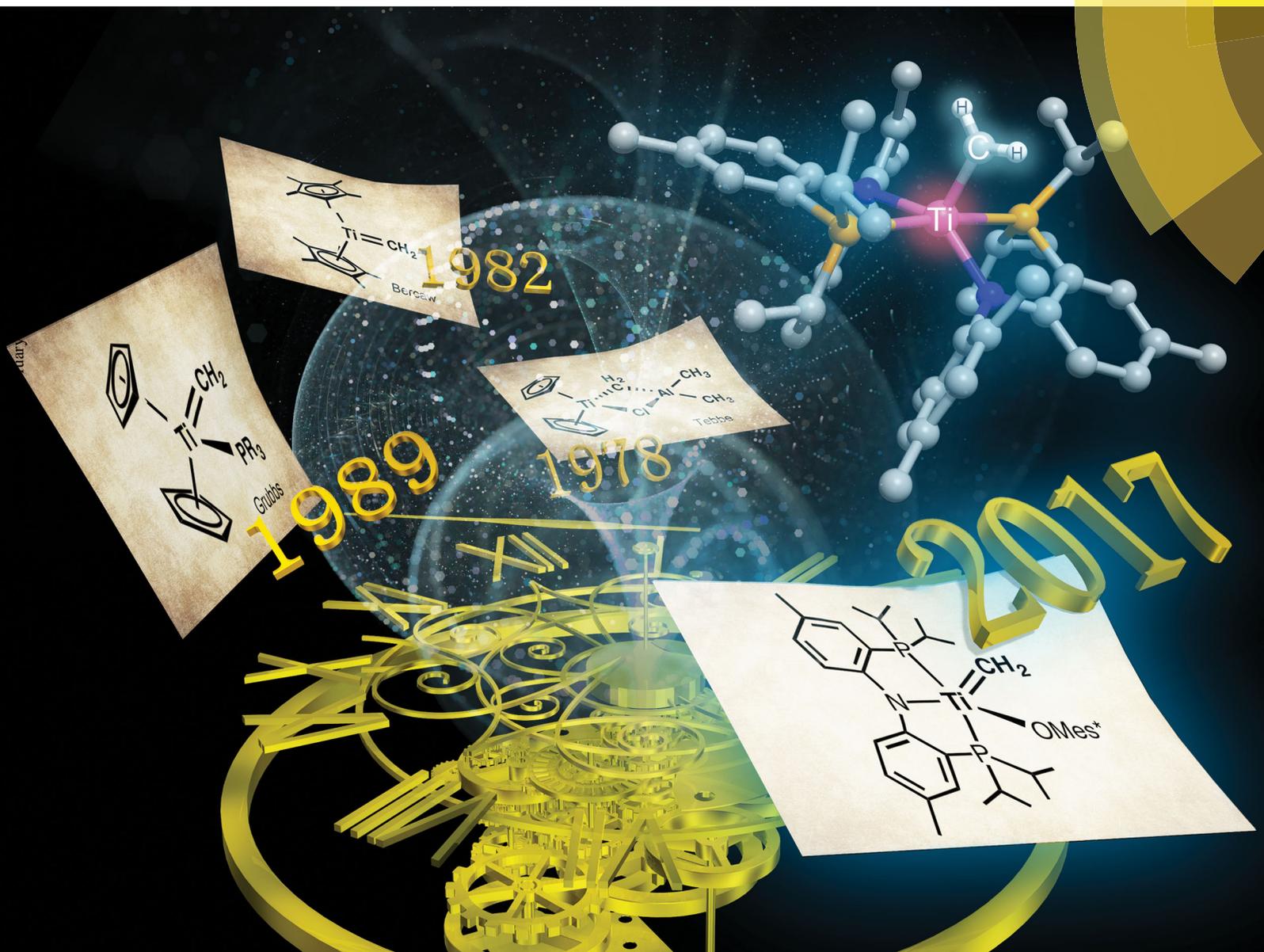


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A radical coupled pathway to a stable and terminally bound titanium methylidene

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Structural elucidation of a mononuclear titanium methylidene†

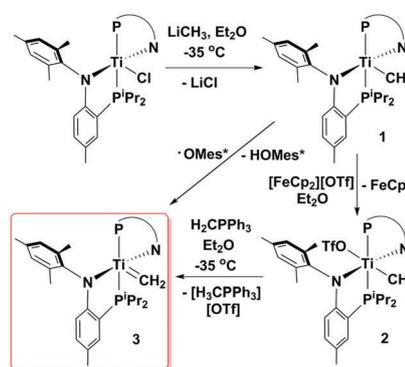
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The first example of a structurally characterized titanium methylidene, $(\text{PN})_2\text{Ti}=\text{CH}_2$, has been prepared *via* one-electron oxidation of $(\text{PN})_2\text{Ti}(\text{CH}_3)$ followed by deprotonation or by H-atom abstraction using an aryloxy radical. The $\text{Ti}=\text{C}$ distance was found to be 1.939(3) Å, and variable temperature, multinuclear, and multidimensional NMR spectroscopic experiments revealed the methylidene to engage in long range interactions with protons on the ligand framework. Computational studies showed that the $\text{Ti}=\text{C}$ bond, which until now has eluded structural studies, displays all the hallmarks of a prototypical Schrock-carbene.

In an entry in his notebook dated July 1974, Frederick Tebbe recorded for the first time the synthesis of the complex $\text{Cp}_2\text{Ti}(\mu_2\text{-CH}_2)(\mu_2\text{-Cl})\text{Al}(\text{CH}_3)_2$.¹ The addition of excess amounts of AlMe_3 to Cp_2TiCl_2 gave a reagent² that has been instrumental in methylidene transfer reactions to carbonyl functionalities presumably *via* a transient $[\text{Cp}_2\text{Ti}=\text{CH}_2]$ species. Appropriately called ‘‘Tebbe’s reagent’’, this complex was also one of the first systems to exchange the methylidene group with olefins and to engage in olefin homologation.^{2–6} Since then, it was found that intermediate $[\text{Cp}_2\text{Ti}=\text{CH}_2]$ can be generated independently by either a thermolytic α -hydrogen abstraction from $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ or by a retro-cycloaddition reaction involving the metallacyclobutane species $\text{Cp}_2\text{Ti}[\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2]$.^{7–10} The transient $[\text{Cp}_2\text{Ti}=\text{CH}_2]$ species can be intercepted in solution at low temperatures using various phosphines by forming $\text{Cp}_2\text{Ti}=\text{CH}_2(\text{PR}_3)$ ($\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PEt}_3$).³ Unfortunately, the inherent reactivity of the $\text{Ti}=\text{CH}_2$ fragment made it impossible thus far to directly characterize the structure of this important moiety.¹¹ In fact, among

the class of Schrock-carbenes, a methylidene with a 3d metal has never been isolated and structurally characterized.¹² Herein we show how a tetragonal environment enforced by two phosphino-anilide ligands can stabilize a Lewis-acid free and terminally bound titanium methylidene, to an extent that it can be formed and thus interrogated spectroscopically, structurally, and computationally.

We recently reported that the scaffold $[(\text{PN})_2\text{Ti}]^{2+}$ ($\text{PN}^- = (N-(2-(\text{diisopropylphosphino})-4\text{-methylphenyl})-2,4,6\text{-trimethylanilide})$) can stabilize terminal nitride and oxo functionalities.^{13,14} However, a methylidene ligand should make the Ti^{4+} center more electron deficient when compared to the isovalent oxo and nitride groups, but it may be comparable to the borylimido complex $(\text{PN})_2\text{Ti}=\text{N}=\text{Bcatechol}$ that we reported recently.¹³ Accordingly, we turned our attention to the precursor $(\text{PN})_2\text{TiCl}$. This complex could be smoothly methylated with LiCH_3 in Et_2O , *via* dropwise addition at -35°C and the solution slowly warmed to room temperature to form the $\text{Ti}(\text{III})$ -methyl complex $(\text{PN})_2\text{Ti}(\text{CH}_3)$ (**1**) in 95% yield as a green colored material (Scheme 1). Complex **1** displays magnetic features in accord with a d^1 species ($\mu_{\text{eff}} = 2.03 \mu_{\text{B}}$, 25°C , Evans method) and the solid state structure confirms the presence of a distorted trigonal-bipyramidal ($\tau_5 = 0.738$)¹⁵



Scheme 1 Two synthetic routes to a mononuclear titanium complex having a terminally bound methylidene.

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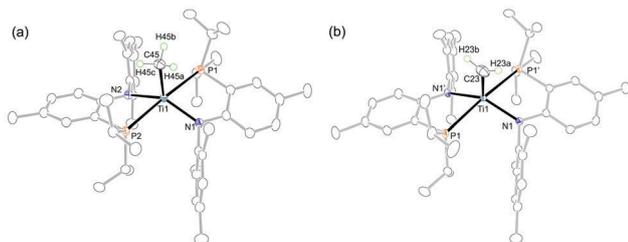


Fig. 1 Solid state structures of (a) complex **1** and (b) complex **3** with thermal ellipsoids at the 50% probability level. H-atoms with the exception of methyl/methylidene hydrogens are excluded for clarity.

Ti(III) species bearing *trans*-phosphine groups ($177.22(3)^\circ$) and a bound methyl group (Fig. 1a). The most salient structural feature, however, is the Ti–C bond length of $2.129(3)$ Å, akin to what has been observed in other five-coordinate Ti(III) derivatives supported by two benzamidinate or β -diketiminato ligands ($\text{PhC}(\text{NSiMe}_3)_2^-$) and $([\text{ArN}(\text{CCH}_3)_2]_2, \text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$.^{16–18} However, unlike the Ti(III) methyl complex reported by Arnold and co-workers, which has a Ti–C–H angle of 105.1° and was reported to have an agostic interaction, we observe no apparent C–H interaction in **1**.¹⁶

Complex **1** can be readily oxidized with $[\text{FeCp}_2][\text{OTf}]$ ¹⁹ in Et_2O to produce the Ti(IV) methyl-triflate $(\text{PN})_2\text{Ti}(\text{CH}_3)(\text{OTf})$ (**2**) in nearly quantitative yield as a bright red colored microcrystalline material (Scheme 1). Although we were unable to obtain solid state structural information for **2**, ^1H , ^{13}C and ^{31}P NMR spectra are consistent with this formulation. Notably, the methyl resonance could be readily located at 1.78 ppm in the ^1H NMR spectrum and correlated to a resonance at 55.1 ppm in the ^{13}C NMR trace by an HMQC NMR experiment. The ^{19}F NMR spectrum showed a resonance at -76.49 ppm in accord with the presence of a OTf^- group, but given the high solubility of **2** in non-polar solvents such as hexanes and arenes, we propose that this ligand is coordinated to the titanium(IV) ion to give a pseudo-octahedral geometry.

Dissolving **2** in Et_2O and treating it with the ylide $\text{H}_2\text{C}=\text{C}(\text{PPh}_3)_2$ ²⁰ at -35°C rapidly produced a colorless precipitate, $[\text{H}_3\text{C}(\text{PPh}_3)_2][\text{OTf}]$, which could be separated from the mixture to leave behind the titanium methylidene $(\text{PN})_2\text{Ti}=\text{CH}_2$ (**3**) as orange crystals in 75% yield subsequent to crystallization from hexanes at -35°C (Scheme 1). Given its extremely reactive nature, formation of **3** is always accompanied by a small amount ($\sim 10\%$) of the methyl species **1**. Applying an HMQC NMR spectroscopic experiment we were able to correlate the downfield shifted signal at 11.82 ppm in the ^1H NMR spectrum to a highly downfield shifted ^{13}C NMR resonance at 291.10 ppm, consistent with the existence of a terminal methylidene ligand. Notably, the methylidene carbon resonance is clearly observed as a triplet of triplets due to $^1J_{\text{CH}} = 124$ and $^2J_{\text{CP}} = 12$ Hz (Fig. 2), whereas the $^{13}\text{C}\{^1\text{H}\}$ NMR experiment collapsed this multiplet resonance into a triplet due to coupling to the equivalent phosphines. Interestingly, the methylidene resonance at 11.9 ppm in the ^1H NMR spectrum experienced multiplicity features that were shown to be due to long range interactions as well as coupling to two nearby benzylic hydrogens with the aid of a NOESY and ^1H – ^1H COSY NMR experiments, respectively (top of Fig. 2). The ^{31}P NMR spectrum is consistent with two equivalent phosphino-anilide ligands in

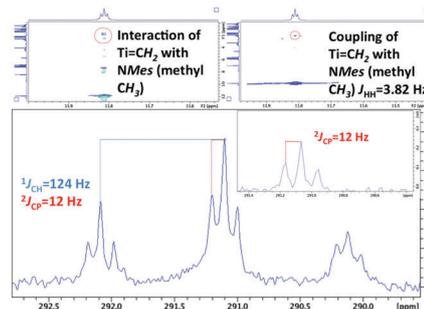


Fig. 2 Top left: NOESY NMR spectrum of **3** featuring interaction of $\text{Ti}=\text{CH}_2$ with NMe_5 ; top right: ^1H – ^1H COSY NMR spectrum of **3** featuring coupling of $\text{Ti}=\text{CH}_2$ with NMe_5 ; bottom: ^{13}C NMR spectroscopic data of **3**, coupled with both ^1H and ^{31}P nuclei. The inset figure features the expanded region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3**.

solution, thus, corroborating the triplet resonance observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (*vide supra*). Remarkably, it was found that complex **3** can be prepared directly in 48% yield *via* H-atom abstraction of **1** with the aryl oxyl radical $^*\text{OMes}^*$ ($\text{Mes}^* = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$).²¹ Based on the average bond dissociation enthalpies²² this reaction is feasible, but the sterically protected nature of the methylidene in **3** and the alcohol byproduct HOMes^* prevent subsequent reactions between the two. The reaction does take several hours to go to completion resulting in some decomposition of **3**.

Single crystals of **3** could be obtained from a concentrated hexanes solution cooled to -35°C , and Fig. 1b depicts the solid state structure of the first terminal Schrock-type methylidene bound to a 3d metal. Akin to the oxo $(\text{PN})_2\text{Ti}=\text{O}$ and nitride salt $[\text{K}(222\text{-kryptofix})][(\text{PN})_2\text{Ti}=\text{N}]$, complex **3** has a $\tau_5 = 0.517$, consistent with a geometry between square-pyramidal and trigonal bipyramidal.¹³ Remarkably, the hydrogen atoms could be located in the electron density map and refined isotropically revealing the π -bond to be oriented along the P–Ti–P plane. Short contacts between the *ortho*-methyl hydrogens on the mesityl and ^iPr methyl moieties of the PN ligand and the methylidene carbon could be observed ($2.7(2)$ and $2.8(6)$ Å). The Ti=C bond length of $1.939(3)$ Å is significantly shorter than that observed for the Ti– CH_3 in **1** but is comparable to structurally characterized 5-coordinate titanium complexes having a substituted alkylidene ligand.^{17,18,23} Complex **3** gradually decomposes at room temperature to form some **1** along with a mixture of other products including CH_4 .

To better understand the electronic structure of the titanium methylidene complex, density functional calculations were carried out on **3**. The coordination geometry that is between square-pyramidal and trigonal bipyramidal motifs is reasonably well reproduced in our calculations with a $\tau_5 = 0.518^{15}$ and a computed Ti=C bond length of 1.868 Å, which is somewhat shorter than what is observed experimentally. Our calculations confirm that there is no agostic interaction between the C–H and the Ti center. Several possible electronic states were considered two of which are discussed: the most natural configuration for a classical Schrock-carbene is the closed-shell singlet state where a formally dianionic $[\text{CH}_2]^{2-}$ ligand interacts with a Ti(IV)- d^0 center. More importantly, we considered its open-shell singlet analogue, where the two

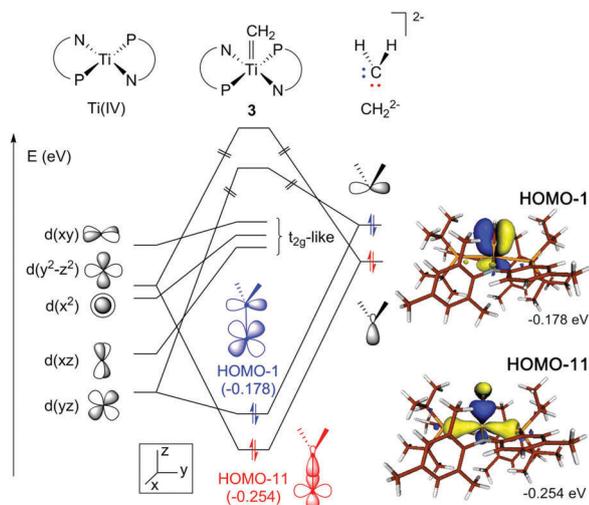


Fig. 3 Qualitative MO-diagram of **3** displaying the molecular orbitals for the σ and π bonds (isodensity value: 0.05 a.u.).

electrons remain in different spatial orbitals, but are spin-paired utilizing a weak antiferromagnetic coupling.²⁴ Such a non-traditional singlet state is experimentally difficult to distinguish from the classical carbene complex. Over the last decade, there has been a growing realization that many small ligands become redox non-innocent and adopt such open-shell configurations.²⁵ Our calculations show, however, that the triplet state of **3** is 14.3 kcal mol⁻¹ higher in energy than the closed-shell singlet, and despite substantial efforts, we were unable to obtain the open-shell singlet state and concluded that it is not a reasonable minimum. Thus, the only stable configuration in the singlet spin state manifold is the classical closed-shell Schrock-carbene state. A Wiberg²⁶ bond order between Ti and C was found to be 1.70, whereas 0.64 is found for the triplet state. Calculations also indicate a significant negative partial charge that remains on the α -carbon and the NBO²⁷ analysis assigned a natural charge of -0.74 to the α -carbon. The qualitative MO-diagram in Fig. 3 illustrates five empty d-orbitals for the Ti(IV)(PN)₂ fragment. When the dianionic [CH₂]²⁻ ligand is added to the axial position, two dominating electronic interactions exist. The first forms the Ti–C σ -bond, where the sp-hybridized donor orbital on the carbene ligand is paired with the d(y²–z²) orbital to afford HOMO–11 at -0.254 eV, as illustrated in Fig. 3. The second important interaction is a dative bond in the π -space from the p-orbital based lone pair on the carbene with a π -acidic d(yz) orbital to form a π -orbital HOMO–1 at -0.178 eV. This interaction determines the parallel orientation of the methyldiene fragment with the P–Ti–P vector. The higher electronegativity of the nitrogen atoms make them better suited to stabilize the π -electrons and the d(yz)-based acceptor orbital becomes more aligned with the N–Ti–N axis. This electronic structure leaves the t_{2g}-like orbitals empty, which establishes a physical oxidation state of Ti(IV)-d⁰, supporting our formal classification mentioned above.

In summary, we have prepared and fully characterized the first example of a titanium methyldiene complex that serves as a

structural analog of the historically important Tebbe's reagent. We speculate the stability of **3** to be a combination of its pseudo tetragonal structure as well as the long-range interactions of the methyldiene ligand with benzylic hydrogens from the PN ligand.

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