Titanium Alkylidenes

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An Alkylidyne Analogue of Tebbe's Reagent: Trapping Reactions of a Titanium Neopentylidyne by Incomplete and Complete 1,2-Additions**

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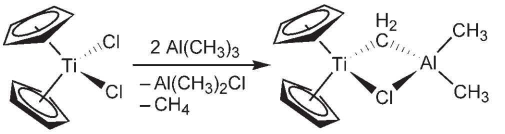
Methylenation of carbonyl-containing functionalities has driven the research of organotitanium reagents for use in organic chemistry.[1,2] Tebbe's reagent, $[Cp_2Ti\{CH_2AlCl(CH_3)_2\}]$ ($Cp = C_5H_5$),[3] a Lewis acid stabilized methylidene complex prepared from addition of two equivalents of $Al(CH_3)_3$ to $[Cp_2TiCl_2]$ [Eq. (1)], was one of the first reported early-transition-metal systems to perform olefin metathesis in a catalytic manner.[4] Hence, it is not surprising that this complex can be often utilized as a Wittig-like reagent for carbonyl methylenation reactions, since it is more reactive than prototypical phospha-Wittig reactants, and works particularly well for sterically encumbered carbonyl groups present in aldehydes, esters, lactones, and amides.[5] It has been argued that the $AlMe_2Cl$ moiety in Tebbe's reagent alleviates the nucleophilic nature of the alkylidene α carbon, thus rendering this reagent far less basic than a Wittig system. Consequently, methylidene-group transfer reactions involving Tebbe's complex and a chiral substrate often do not result in epimerization of the product.[5] Although Tebbe's reagent was first prepared almost 30 years ago, examples of an alkylidyne analogue for this seminal species have remained elusive, presumably because of the incipient negative charge confined at the Ti≡C multiply bonded α-carbon atom.



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Herein we report that an alkylidyne moiety in [(PNP)Ti≡C*t*Bu] (**A**; PNP = [2-{P(CHMe$_2$)$_2$}-4-methylphenyl]$_2$N$^-$), generated from [(PNP)Ti=CH*t*Bu(CH$_2$*t*Bu)] (**1**),[6] can be conveniently stabilized with $Al(CH_3)_3$ to afford the first example of a Lewis acid stabilized Group 4 alkylidyne [(PNP)Ti{C(*t*Bu)Al(CH$_3$)$_3$}] (**2**). Our studies suggest that $Al(CH_3)_3$ likely accelerates α-hydrogen abstraction in the process of making compound **2**. We also demonstrate that complex **2** is remarkably stable, but in the presence of pyridine behaves as an alkylidyne analogue of Tebbe's reagent, thus cleanly ring opening the strong C–N bond of the N-heterocycle. During the course of our studies we discovered that complex **1** can cleave the B–O bond of the Lewis acid $B(OCH_3)_3$ to afford an unusual titanium complex containing an alkylidene ligand substituted with an electrophilic motif $-B(OCH_3)_2$. The solid state structures for the zwitterionic species [(PNP)Ti{C*t*BuAl(CH$_3$)$_3$}] as well as the product resulting from B–O bond cleavage across the Ti≡C moiety in **A** are also presented and discussed.

Our inability to trap the alkylidyne moiety in **A** by addition of Lewis bases, such as PR_3 ($R = CH_3$, Ph), THF, HMPA (hexamethyl phosphoramide), $OP(CH_3)_3$, and pyridines,[7,8] prompted us to investigate whether the nucleophilic nature in the Ti≡C linkage could be sequestered by a Lewis acid, such as $Al(CH_3)_3$. Tebbe and co-workers reported an analogous reaction involving $[Cp_2Ti(CH_3)_2]$ and $Al(CH_3)_3$ to afford $[Cp_2Ti\{CH_2Al(CH_3)_3\}]$, which was characterized spectroscopically.[3] However, this zwitterion was never generated in pure form and was contaminated by residual dimethyl precursor.[3] We treated compound **1**[6] with neat or stoichiometric $Al(CH_3)_3$, at low temperatures, which resulted in immediate formation of the zwitterionic complex [(PNP)Ti{C(*t*Bu)Al(CH$_3$)$_3$}] (**2**) concurrent with CH$_3$*t*Bu extrusion.[9] Complex **2** has been characterized by ^{1}H, ^{13}C, ^{31}P, and ^{27}Al NMR spectroscopy, elemental analysis, as well as by single crystal X-ray diffraction studies.[9] Whereas the ^{31}P NMR spectrum clearly suggests **2** to have C_1 symmetry in solution (two doublets, $J_{PP} = 36$ Hz), the ^{1}H NMR spectrum displays three inequivalent methyl resonances for the $Al(CH_3)_3$ moiety in **2**, consistent with the two terminal $Al(CH_3)_2$ methyl groups being diastereotopic owing to the skewed symmetry of the PNP aryl framework.[6,9] This diagnostic signature confirms that a rigid Ti–C–Al–C four-membered ring in **2** is preserved in solution at room temperature. Interestingly, the ^{13}C and ^{13}C{^{1}H} NMR spectrum of **2** reveals a resonance at $\delta = 333.0$ ppm for a highly deshielded carbon atom, which is consistent with a Ti–C multiply bonded functionality. This resonance does not couple directly to a hydrogen atom. Notably, the low-temperature ^{27}Al NMR spectrum of **2** (−40 °C) showed a broad resonance at $\delta = 56.8$ ppm ($\Delta\nu_{1/2} = 5890$ Hz), and upon warming the probe to 45 °C,

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a second but minor resonance at $\delta = 195.1$ ppm emerged with $\Delta\nu_{1/2} = 5417$ Hz.[9] Cooling the solution again to low temperature caused the second resonance to vanish, thus hinting that another species might be equilibrating with **2** upon warming.

A structural analysis for **2** (Figure 1)[10] unambiguously portrays an unperturbed {(PNP)Ti} unit containing a remarkably short Lewis acid stabilized alkylidyne moiety (Ti–C, 1.825(2) Å),[11] which is bridged by a {AlCH$_3$} unit to furnish a puckered, four-membered alatitanacyclobutene. Intuitively, complex **2** originates from coordination of Al(CH$_3$)$_3$ to the nucleophilic alkylidyne carbon in putative **A** (Scheme 1). Alternatively, formation of **2** can be viewed as an incomplete 1,2-Al–C addition across the Ti≡C functionality in **A** to yield a long Al–CH$_3$ bond for the bridging group (2.079(2) Å) compared to the terminal Al–CH$_3$ group (ca. 1.98 Å). Congruently, bridging of the methyl group results in a comparatively long Ti–CH$_3$ (2.293(3) Å) bond, when such a distance is compared to terminal Ti–C$_{\text{alkyl}}$ linkages in similar compounds, such as [(PNP)Ti=CH*t*Bu(R)] (R = Ph, 2.141(5) Å; CH$_2$*t*Bu, 2.206(5) Å).[6]

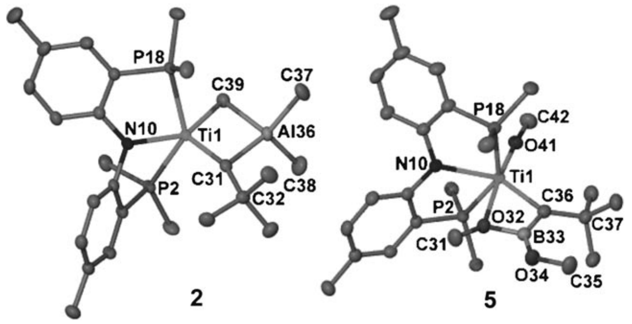
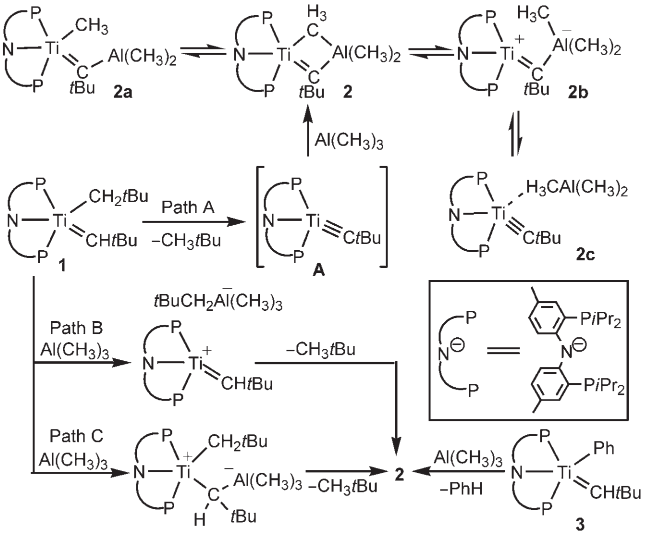


Figure 1. Molecular structures of **2** (left) and **5** (right), with thermal ellipsoids set at 50% probability. Hydrogen atoms and isopropyl methyl groups on the phosphorus atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **2**: Ti1-C31 1.825(2), Ti1-N10 2.057(1), Ti1-C39 2.293(3), Ti1-P2 2.5900(4), Ti1-P18 2.6751(4), Ti1-Al36 2.6695(4), C39-Al36 2.136(4), C31-Al36 2.079(2), Al36-C37 1.975(5), Al36-C38 1.981(5), P2-Ti1-P18 140.77(3); C39-Ti1-C31 101.02(5), C39-Al36-C31 98.46(5). For **5**: Ti1-O41 1.787(4), Ti1-C36 1.976(2), Ti1-O32 2.206(4) Ti1-N10 2.243(6), Ti1-P2 2.5738(6), Ti1-P18 2.5872(6), B33-C36 1.514(3); P2-Ti1-P18 147.01(2), C37-C36-Ti1 137.6(5).



Scheme 1. Formation of complex **2** by Path A (upper); possible isomeric structures of **2** are depicted. Also portrayed (lower) is the formation of complex **2** from **1** (by Path B or C)or **3** by addition of Al(CH$_3$)$_3$. See text for details.

Based on the above metrical parameters, several isomeric structures could be proposed for **2** resulting from complete or incomplete methide transfer between aluminum and titanium (**2** and **2a**, Scheme 1, upper left), or from adduct formation (structures **2b** and **2c**, Scheme 1, upper right). Whereas the reactivity of isomer **2b** is questionable, isomer **2a** is best described as an alkylidene analogue and should display chemistry more closely to that of a Ti=C functionality. Isomer **2c** on the other hand is more likely to expel Al(CH$_3$)$_3$, forming **A**, and should thus react like an alkylidyne. However, **2c** was found to be 37 kcal mol^{-1} higher (by DFT methods) in energy than the other two isomers.[9]

Natural bond order (NBO) calculations agree well with our proposed connectivity for the resting-state geometry in **2**. The computed Ti1–C31 NBO is 2.04, a value confined between a bond order of two (1.74) and three (2.49), both of which we have previously reported.[8] On the other hand, the Al36–C31 NBO is 0.48, suggesting a weaker linkage than a terminal Al–CH$_3$ bond (NBO for Al36–C37, 0.92; for Al36–C38, 0.91). As implied by the bond lengths in the solid-state structure of **2**, the Ti1–C39 NBO is 0.57 and Al36–C39 is 0.37. Hence, the interaction of the bridging methyl group is weak for both titanium and aluminum and best reflects an incomplete addition by formation of an ionic species. Further examination of the electronic structure of **2** shows that the HOMO is a π orbital composed of the Ti=C bond, and the LUMO is consistent with a d^0 Ti d$_{xy}$ nonbonding orbital (Figure 2). However, HOMO−2 can be recognized as a slipped σ bond involving the Ti d$_{z^2}$ and C31 p$_x$ orbitals, whereas the HOMO−6 is best viewed as being a lone pair

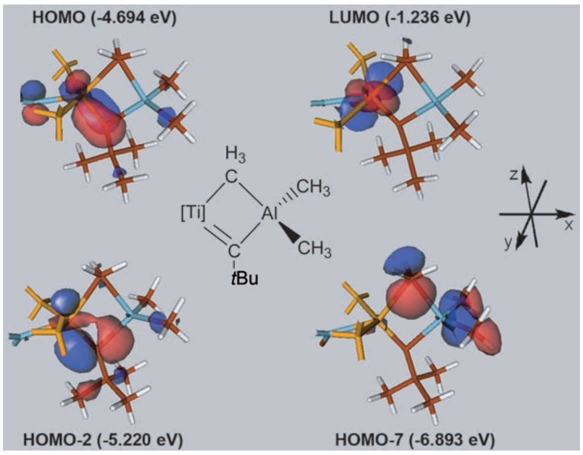


Figure 2. Most important molecular orbitals of the Ti-C31-Al-C39 metallacycle core of **2** (isodensity = 0.05 au). Red C, white H, yellow Ti and P, light blue Al and N. Only the P and N atoms of the PNP ligand are shown for clarity.

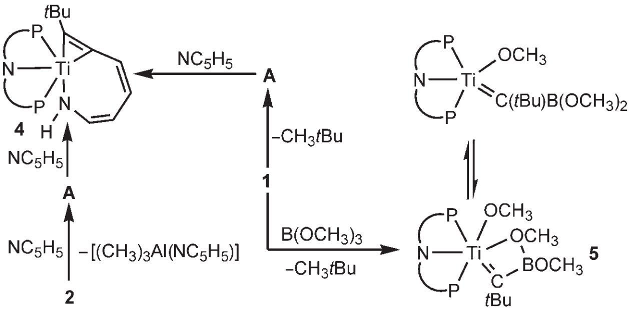
of electrons originating from C39. As a result, the bridging methyl group in **2** can be considered more as an ionic interaction—weaker than normal Al–C bonds, whereas the Ti1–C31 bond has stronger Ti–C interactions than a generic Ti=C bond.

As noted above, formation of **2** might proceed by incomplete 1,2-Al– addition of $Al(CH_3)_3$ across the Ti≡C linkage of putative **A** (Scheme 1, Path A). However, alkyl abstraction in **1** by $Al(CH_3)_3$ could also result in formation of an alkylidene cation concurrent with formation of the super-basic ion $[Al(CH_2tBu)(CH_3)_3]^-$ (Scheme 1, Path B). This superbase would then ensue generation of **2** by α-deprotonation. Schrock and Sharp have proposed a similar pathway in the formation of a $[Cp_2Ta\{CH_2Al(CH_3)_3\}(CH_3)]$.[12] Alternatively, the assembly of **2** could also proceed by addition of $Al(CH_3)_3$ to the nucleophilic alkylidene carbon in **1** followed by α-hydrogen abstraction (Scheme 1, Path C). As formation of **2** from **1** and $Al(CH_3)_3$ is rapid (after several seconds the reaction is complete), we propose that $Al(CH_3)_3$ does in fact promote elimination of CH_3tBu given that the $t_{1/2}$ for **1** in benzene is much slower with a value of 3.1 h at 25 °C ($k_{avg} = 6.5(4) \times 10^{-5}\,s^{-1}$).[6]

We also found that compound **2** can be prepared from [(PNP)Ti=CH*t*Bu(Ph)] (**3**) and $Al(CH_3)_3$ over several minutes at 25 °C (Scheme 1).[6] These results imply that the Lewis acid accelerates α-hydrogen abstraction in precursors **1** and **3**, especially since the latter precursor can only equilibrate to **A** in benzene under forcing conditions (95–120 °C) with a $k_{avg} = 1.2(2) \times 10^{-5}\,s^{-1}$.[6] As a result, we speculate that Paths B and C are operative in these reactions, and that a naked alkylidyne intermediate, Path A, is not generated in these reactions.

To test whether **2** is indeed an alkylidyne synthon, we investigated several substrates that would react cleanly with **1** via a transient alkylidyne intermediate. Unfortunately, complex **2** is remarkably stable at temperatures above 80 °C for 2 days in C_6H_6,[6] and in the presence of nitriles,[13] which is in stark contrast to **1**. In the presence of Lewis bases, such as quinuclidine, HMPA, and phosphines, complex **2** slowly decomposes at >90 °C, but to a myriad of intractable products. However, treatment of **2** with excess pyridine at 40 °C over 2 days results in quantitative conversion into the known azametallabicyclic compound $[(PNP)Ti\{C(tBu)CC_4H_4NH\}]$ (**4**)[8] and the adduct $[(CH_3)_3Al(NC_5H_5)]$ (Scheme 2).[9] The ring-opened pyridine complex **4** can be prepared independently from **1** in neat pyridine, and the results of mechanistic studies are in accordance with intermediate **A** being generated along the reaction coordinate.[8] This result does support the notion that **2** is a synthon to **A**, but only when the reagent can sequester the Lewis acid while simultaneously acting as a substrate for the nucleophilic {Ti≡C*t*Bu} ligand.

Milder electrophiles also react with **1**, but result instead in complete 1,2-addition. For example, treatment of **1** with $B(OCH_3)_3$ causes a rapid color change from green to red, concurrent with formation of the alkylidene methoxide complex $[(PNP)Ti\{C(tBu)B(OCH_3)_2\}(OCH_3)]$ (**5**; Scheme 2).[9] The solid-state structure of **5** (Figure 1)[14] is a six-coordinate Ti^{IV} alkylidene species (Ti=*C*, $\delta = 323.7$ ppm),



Scheme 2. Synthesis of complexes **4** and **5** from compounds **2** and **1**, respectively.

in which of one of the methoxy groups has migrated from boron to the metal center.[14] As a result, the alkylidene carbon has accepted a $B(OCH_3)_2$ group (^{11}B NMR spectroscopy: $\delta = 40.2$ ppm, $\Delta\nu_{1/2} = 11\,692$ Hz). Based on the molecular structure of **5**, all the $-OCH_3$ groups should be inequivalent, given the skewed orientation of each inequivalent phosphorus arm (^{31}P NMR spectrum: two doublets with $J_{PP} = 47$ Hz). However, the ^{1}H NMR spectrum of **5** implies that the interaction suggested by the solid-state structure is fluxional; the spectrum indicates only two inequivalent $-OCH_3$ groups in a 2:1 ratio (Scheme 2). The solid-state structure of **5** (Figure 1) has a Ti–C bond (1.976(2) Å) which is longer than other titanium alkylidene linkages reported with this ligand.[6,7,11b] This elongation could be the result of a higher coordination environment about the metal center. Most notably, the alkoxide distance (Ti1–O41, 1.787(4) Å) is much shorter than the dative Ti1–O32 interaction (2.206(4) Å).

In conclusion, the Lewis acid stabilized titanium alkylidyne **2**, analogous to Tebbe's reagent, was prepared and structurally characterized. In the presence of pyridine, **2** extrudes the $Al(CH_3)_3$ protecting group, thus behaving as a naked titanium alkylidyne, ultimately ring opening the N-heterocycle. As opposed to incomplete 1,2-addition of $Al(CH_3)_3$ across the the Ti≡C linkage, milder electrophiles, such as $B(OCH_3)_3$, break apart to form an unprecedented titanium alkylidene incorporating the $-B(OCH_3)_2$ moiety.

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[9] See Supporting Information for complete experimental details.

[10] Crystal data for **2**: $C_{34}H_{58}AlNP_2Ti$, $M_r = 617.63$, triclinic, space group $P\bar{1}$, $a = 10.9247(8)$, $b = 11.6164(8)$, $c = 14.3622(10)$ Å, $\alpha = 93.013(2)$, $\beta = 97.780(2)$, $\gamma = 97.587(2)°$, $Z = 2$, $\mu = 0.376\ \text{mm}^{-1}$, $\text{Mo}_{K\alpha} = 0.71073$ Å, $V = 1785.4(2)$ Å^3, $T = 125(2)$ °C, $\rho_{\text{calcd}} = 1.149\ \text{mg mm}^{-3}$, GoF on $F^2 = 1.031$, $R_1 = 3.39\%$ and $wR_2 = 8.25\%$ (F^2, all data). Out of a total of 45767 reflections collected, 8215 were unique and 7094 were observed ($R_{\text{int}} = 4.82\%$) with $I > 2\sigma I$ (red-pink prism, $0.30 \times 0.30 \times 0.20\ \text{mm}^3$, $27.48° \geq \Theta \geq 2.21°$). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.[15]

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[14] Crystal data for **5**: $C_{34}H_{58}BNO_3P_2Ti{\cdot}0.25\,C_5H_{12}$, $M_r = 686.73$, monoclinic, space group $P2_1/n$, $a = 11.5558(6)$, $b = 21.5062(11)$, $c = 16.1661(8)$ Å, $\beta = 106.3710(10)°$, $Z = 4$, $\mu = 0.339\ \text{mm}^{-1}$, $\text{Mo}_{K\alpha} = 0.71073$ Å, $V = 3854.7(3)$ Å^3, $T = 125(2)$ °C, $\rho_{\text{calcd}} = 1.183\ \text{mg mm}^{-3}$, GoF on $F^2 = 1.103$, $R_1 = 6.39\%$ and $wR_2 = 12.20\%$ (F^2, all data). Out of a total of 114062 reflections collected, 8834 were unique and 6839 were observed ($R_{\text{int}} = 6.25\%$) with $I > 2\sigma I$ (red-brown block, $0.25 \times 0.25 \times 0.25\ \text{mm}^3$, $24.80° \geq \Theta \geq 2.23°$). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. A partial occupancy pentane was present in the cell.[15]

[15] CCDC-650732 (**2**) and CCDC-650733 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.