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Structural Elucidation of the Illustrious Tebbe Reagent

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Ⓢ *Supporting Information*

ABSTRACT: The Tebbe reagent, $[Cp_2Ti(\mu_2\text{-}Cl)(\mu_2\text{-}CH_2)AlMe_2]$ (**1**), has finally been structurally characterized due to the fortuitous formation of cocrystals of **1** and $[Cp_2Ti(\mu_2\text{-}Cl)_2AlMe_2]$ (**2**). Single crystals of **1** and **2**, despite being extremely reactive and forming an amorphous white coat, can be mounted and data collected to high resolution, thereby providing for the first time a solid-state representation of a titanium methylidene adduct with diphilic $AlClMe_2$.
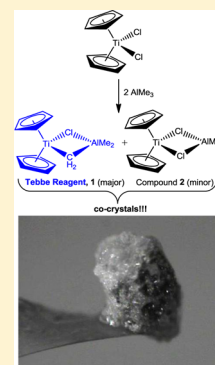
The Tebbe reagent,[1] $[Cp_2Ti(\mu_2\text{-}Cl)(\mu_2\text{-}CH_2)AlMe_2]$ (**1**), stands as a historic milestone in the field of organometallic chemistry. Its ability to transfer a methylene group to organic species via metallo-Wittig chemistry was later extended to other methylidene transfer reactions[2−5] which proceed through a similar metathesis. This well-known process ultimately culminated in the 2005 Nobel Prize being awarded to Chauvin, Grubbs, and Schrock.[6−8] Although reagent **1** was first reported by Tebbe and co-workers in 1978,[9] the original experiments were performed much earlier in the summer of 1974 at the DuPont Central Research Division.[10] Compound **1** is prepared readily, under an inert atmosphere, by addition of a slight excess of $AlMe_3$ to Cp_2TiCl_2 in toluene in yields ranging from 80 to 90% (eq 1).[9] In the presence of a suitable Lewis base, **1**
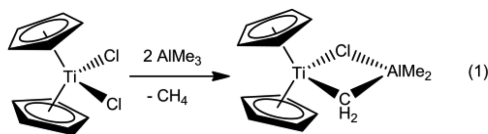
can be a source of the transient methylidene $[Cp_2Ti=CH_2]$,[11] the species responsible for metallo-ylide group transfer. As originally noted by Tebbe, compound **1** can be readily isolated in pure form by crystallization of the mixture from a toluene/pentane solution (the temperature was not specified in the original work).[9] Compound **1** slowly degrades in the solid-state at room temperature, while solids or solutions both rapidly produce methane in the presence of air. Species **1** is well-known in the context of organic and inorganic chemistry; however, structural characterization has remained elusive, presumably due to its reactive nature or difficulties associated

with producing single crystals. In this note, we report high-quality X-ray data of **1** (grown as a cocrystal with an impurity) and discuss a high-resolution solid-state structure confirming the original geometry proposed by Tebbe.[9] For the first time, and nearly 40 years after Tebbe's ground-breaking experiment, we provide here precise geometrical parameters for the structure of Tebbe's reagent. Additionally, structural and spectroscopic data for a side product in the synthesis is reported.

In 1980, Tebbe and co-workers reported the molecular structure of a close analogue, $[Cp_2Ti(\mu_2\text{-}Cl)(\mu_2\text{-}CH_2)Al(CH_2tBu)_2]$, obtained via alkyl exchange of **1** with $[Al(CH_2tBu)_3]$.[12] Unfortunately, the solid state structure of the neopentyl analogue suffers from occupancy disorder confined between the bridging chloride and methylidene group. Consequently, positions were refined for chloride and methylene, resulting in average distances of 2.494(1) and 2.380(2) Å to the titanium, respectively. The corresponding distances to the aluminum are reported as 2.258(2) and 2.213(2) Å, although it is possible that the average bridging atom positions of a cocrystal could also be refined. Thus, the X-ray structure and the NMR results only verify the overall gross geometry, showing the formation of a methylidene species whereby the CH_2 and/or Cl bridge the Cp_2Ti and R_2Al fragments.[12] Structural confirmation of **1** has not been documented,[10] despite it being the first group 4 alkylidene, the first alkyl complex with both a transition metal and Al, and most notably, one of the first systems to engage in metathesis

reactions resulting in the formation of many organic molecules, including natural products.[5] Therefore, we tenaciously explored, under various conditions, structural studies of single crystals of **1**. In this report we discovered that the presence of a cocrystal allows for reliable diffraction data on a single crystal and show that an impurity accompanies this reagent.

Following Tebbe's original protocol,[9] complex **1** was prepared on a smaller scale in toluene using 2.0 g of the precursor Cp_2TiCl_2 and a 2 M hexanes solution of $AlMe_3$. Evaporation of the solvent, extraction of the oily red residue in neat pentane (as opposed to a toluene/pentane solution), and cooling of the solution to −25 °C over 19 days resulted in the formation of large, blood red blocks of what appeared to be pure **1**. The ^{1}H and ^{13}C NMR spectra of a batch of crystals appear to be consistent with pure **1**.[9] Because of the highly reactive nature of the crystals, numerous attempts to mount them on the goniometer resulted in rapid decay of the sample and loss of diffraction quality.[13] To impede decomposition of the sample, a slide containing **1** was prepared in a glovebox with perfluorinated oil and placed in a Teflon-cap-sealed vessel. During transport and handling, great care was taken to keep the sample cold using a secondary container of dry ice. Crystals were selected from the open slide placed on dry ice. Upon removal from the original container, the surface of the dark red crystals began to bubble violently, causing the majority of them to decompose to a colorless, amorphous solid. A particularly large crystal was chosen, part of the decomposition product was quickly removed, and the specimen was capped with a precooled cryovial and transported to the goniometer and mounted under a nitrogen cold stream (150 K). In spite of considerable decomposition on the surface of the crystal (Figure 1, left) very strong single diffractions were observed well beyond 60° in 2θ (Figure 1, right).
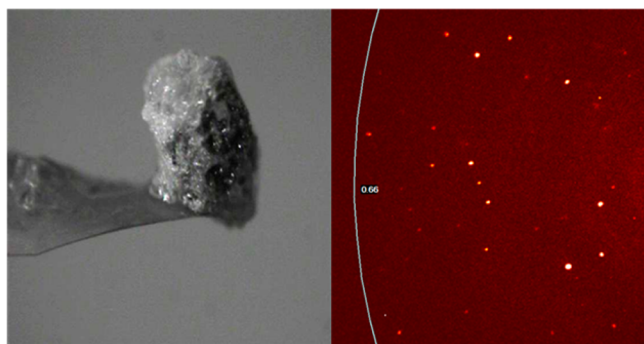

Figure 1. (left) Single crystal of **1** coated with decomposition material. (right) Example frame showing excellent diffraction.

For the particular specimen chosen, a standard structure solution revealed a cocrystal of $[Cp_2Ti(\mu_2\text{-Cl})(\mu_2\text{-CH}_2)AlMe_2]$ (**1**) and $[Cp_2Ti(\mu_2\text{-Cl})_2AlMe_2]$ (**2**). This cocrystallization manifests itself in a disorder of one of the bridging positions with a site occupancy of the major component **1** of 0.62 (Figure 2).[14] A single constraint for equal anisotropic displacement parameters was used for C13 and Cl2. The hydrogen atoms of C13 could be located in the Fourier difference map; however, they were ultimately refined as "riding atoms" in calculated positions.

The formation of **2** is consistent, in part, with the original report by Krusic and Tebbe,[15] which invoked the transient $[Cp_2TiCl]$ being produced en route to the mixed-valent
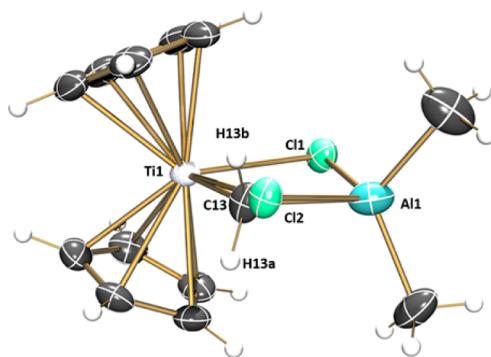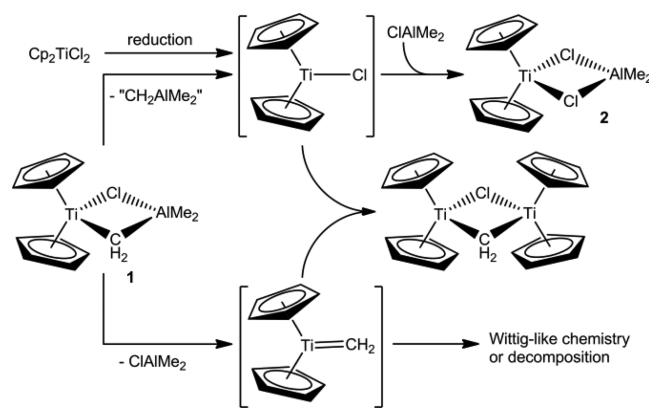

Figure 2. Cocrystallization of complexes **1** and **2** showing the positions of the modeled methylidene in **1** and chloride in **2**.

dinuclear species $[Cp_2Ti(\mu_2\text{-CH}_2)(\mu_2\text{-Cl})TiCp_2]$ (Scheme 1). Repeating the conditions originally reported,[15] a room-

Scheme 1. Proposed Decomposition Pathway of the Tebbe Reagent

temperature X-band EPR spectrum of single crystals further confirmed the presence of **2**.[16] A ^{1}H NMR spectrum of single crystals of **1** and **2** reveals approximately 58% of the former when using a known amount of an internal standard, therefore suggesting that **2** must be present in significant quantities. Notably, some of the side product **2** can be separated by careful fractional crystallization from toluene at −27 °C.[13] Therefore, formation of **2** most likely involves trapping of $[Cp_2TiCl]$ by $AlClMe_2$, and such a process might be catalyzed by a trace amount of Lewis base. The origin of $[Cp_2TiCl]$ is unknown, and such a species could form from **1** or by reduction of the precursor Cp_2TiCl_2 (Scheme 1).[17]

The solid-state structure of **1** (with compound **2** omitted for clarity), shown in views from the front and the top (Figure 3), depicts a titanocene motif possessing bridging chloride and methylidene to an $AlMe_2$ fragment. The Cp_{cent}–Ti–Cp_{cent} angle (134.0°) is comparable to those in $[Cp_2Ti(\mu_2\text{-Cl})(\mu_2\text{-CH}_2)Al(CH_2tBu)_2]$ (132.31°)[12] and Cp_2TiMe_2 (134.54°)[12] However, the most notable feature is the methylidene–Ti distance (2.095(5) Å), which is significantly shorter than the disordered methylidene distance reported for $[Cp_2Ti(\mu_2\text{-Cl})(\mu_2\text{-CH}_2)Al(CH_2tBu)_2]$ (2.3805(5) Å).[12] This distance is slightly longer than that observed for both bridging ethylidene (1.933(6) Å)[18] and terminal alkylidene complexes of titanium (1.884(4) Å)[19] but akin to that of bridging vinylidene complexes (2.023(5) Å).[20]
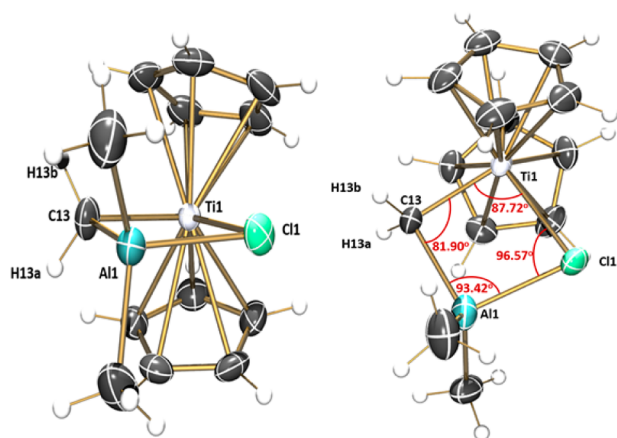
Figure 3. Molecular structure (two perspective views) of **1**. Selected bond distances (Å) and angles (deg): Ti1−C13 = 2.095(5), Ti1−Cl1 = 2.5585(7), Al1−C13 = 2.167(7), Al1−Cl1 = 2.2854(9); Al1−Cl1−Ti1 = 81.90(3), C13−Al1−Cl1 = 93.43(15), Ti1−C13−Al1 = 96.5(2), C13−Ti1−Cl1 = 87.7(2).

After almost 40 years after its discovery, we have found that a slight modification of Tebbe's original protocol—crystallizing compound **1** directly from pentane instead of toluene—results in the fortuitous formation of high-quality single cocrystals of **1** and **2**, therefore allowing us to obtain for the first time a reliable snapshot of the molecular structure of the Tebbe reagent along with a side product. The latter is apparently innocuous to the reactivity of the transient methylidene, since it is likely present in small amounts when solutions of **1** are prepared in situ.[21] However, the single crystals obtained from our synthesis reveal species **1** to be present in 58% yield based on mass, therefore implying that **2** must be present in the crystals in significant quantities. We have shown that a combination of NMR and EPR spectroscopic data confirm the formation of **1** (major) and **2** (minor) as products composing the crystalline material, almost in similar ratios.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Text, figures, tables, and a CIF file giving detailed experimental procedures, crystallographic data,[22] mounting of single crystals of cocrystals of **1**/**2**, crystal structure collection, structure solution, and refinement data for complex **1**, crystallographic parameters, and an EPR spectrum of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(14) Crystallographic details for **1** and **2**: a dark red crystal of approximate dimensions 0.30 × 0.29 × 0.24 mm³ was placed onto the tip of a 0.10 mm diameter MiTeGen pin and mounted on a Bruker APEX II Kappa Duo diffractometer equipped with an APEX II detector at 150(2) K. A total of 33941 reflections (−29 ≤ h ≤ 31, −16 ≤ k ≤ 16, −21 ≤ l ≤ 21) were collected in the range 2.04−30.05°, 4887 of which were unique (R_{int} = 0.0422); Mo Kα radiation was used (λ = 0.71073 Å). 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 to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with aniosotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The residual peak and hole electron densities were 0.369 and −0.658 e Å⁻³. The absorption coeffiecient was 0.773 mm⁻¹. The least-squares refinement converged normally with residuals of R1 = 0.0435, wR2 = 0.0965 and GOF = 1.209. Crystal data: $C_{16.12}H_{21.23}AlCl_{1.38}Ti$, C2/c, a = 22.4504(8) Å, b = 11.9176(4) Å, c = 15.2004(10) Å, α = 90.00°, β = 124.8580(10)°, γ = 90.00°, V = 3337.2(3) Å³, Z = 8, ρ_{calcd} = 1.349, F(000) = 1411.

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(22) CCDC-955969 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.

cam.ac.uk/conts/retrie-ving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).