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Notes

Stable Methylene- and Oxo-Bridged Monocyclopentadienyl Titanium Compounds. Molecular Structure of $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2-O)]Me\}_2(\mu-CH_2)$[†]

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Summary: Thermolysis of $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2-O)]Me_2\}_2$ *affords the methylene-bridged titanium compound* $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2-O)]Me\}_2(\mu-CH_2)$*, concurrent with the evolution of methane, the first example of a fully characterized homometallic cyclopentadienyl titanium* μ*-methylene derivative. Reaction of the* μ*-methylene compound with water affords the isostructural* μ*-oxo complex* $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2-O)]Me\}_2(\mu-O)$*. Reaction of the geminal dititanium methylene complex with benzophenone is also studied.*

Introduction

Alkylidene complexes of group 4 metals play a significant role in important catalytic and stoichiometric processes.[1] Surface-bound methylene species have been postulated to be key intermediates in heterogeneous Fischer−Tropsch chemistry.[2] In this regard, methylene-bridged complexes have been envisaged as models for surface methylene species.[3] In addition, the most widely studied example, methylidene titanocene $[Cp_2Ti{=}CH_2]$, is generated in situ from the heterodinuclear μ-methylene complex $[Cp_2Ti(\mu-CH_2)(\mu-Cl)AlMe_2]$ (Tebbe reagent).[4] Despite the strong interest in this field, and in contrast to groups 5 and 6,[5] stable and well-characterized group 4 metal methylene and alkylidene complexes are rare (particularly in the case of titanium).[6]

In our studies on dinuclear complexes we have reported that the cooperative effect exerted on simple molecules by two close reactive metal centers offers a valuable synthetic strategy to accomplish unusual coordination modes and stabilize highly reactive fragments.[7−9] Herein we establish that the complex $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2-O)]Me_2\}_2$[10] (**1**) exhibits favorable prerequisites for the preparation of the first example of a stable and crystallographically characterized methylene-bridged titanium compound bearing a cyclopentadienyl ligand formed via an α-hydrogen abstraction process. The hydrolysis reaction of this *geminal* dititanium methylene complex is also reported.

Results and Discussion

The reaction of $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2-O)]Cl_2\}_2$ (**1**) with a stoichiometric amount of MgClMe affords the tetramethyl derivative $\{Ti[\mu-(\eta^5-C_5Me_4SiMe_2-O)]Me_2\}_2$ (**2**) in good yield, which can be stored indefinitely at room temperature, under inert atmosphere, without ap-

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[†] Dedicated to Professor José Vicente Soler on the occasion of his 60th birthday.

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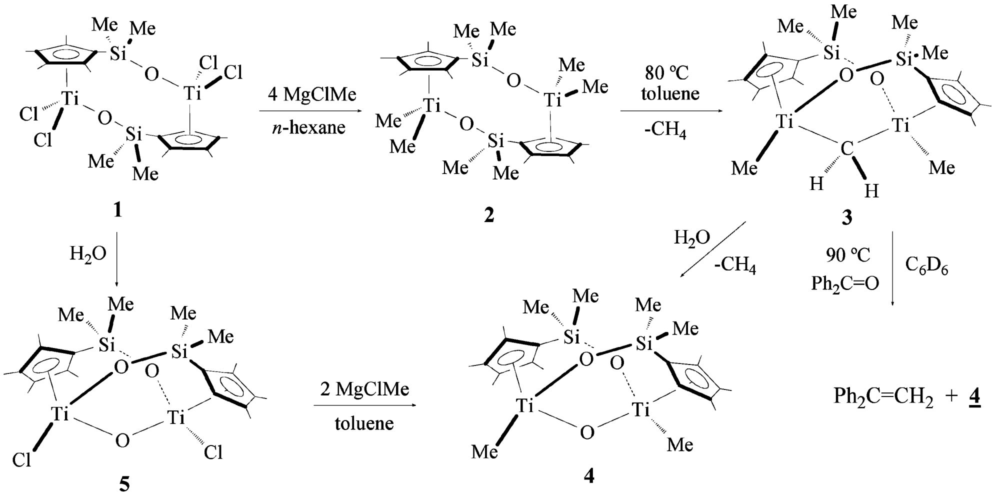
Scheme 1



preciable decomposition, either in the solid state or in solution.[10] However, upon heating to 80 °C in toluene solution, **2** is transformed, via the activation of a methyl C−H bond, to a new compound, identified as the methylene-bridged titanium complex $\{Ti[\mu\text{-}(\eta^5\text{-}C_5Me_4SiMe_2\text{-}O)]Me\}_2(\mu\text{-}CH_2)$ (**3**) (Scheme 1). Complex **3** is isolated in good yield as a yellow crystalline solid. Monitoring the thermolysis of **2** by NMR in benzene-d_6 reveals gradual clean formation of **3**, concurrent with the evolution of 1 equiv of methane. However, prolonged warming causes full decomposition, affording a mixture of unidentified paramagnetic species.

Complex **3** is very moisture sensitive, and the presence of traces of water results in the evolution of 1 equiv of methane, affording the isostructural oxo-bridged complex $\{Ti[\mu\text{-}(\eta^5\text{-}C_5Me_4SiMe_2\text{-}O)]Me\}_2(\mu\text{-}O)$ (**4**). Such transformations can be seen as resulting from the replacement of the bridging methylene group by the isoelectronic μ-oxo functionality. Compound **4** may be alternatively synthesized by alkylation of the previously reported[10] μ-oxo chloro $\{Ti[\mu\text{-}(\eta^5\text{-}C_5Me_4SiMe_2\text{-}O)]Cl\}_2(\mu\text{-}O)$ derivative. Reaction of the μ-oxo chloro compounds with 2 equiv of MgClMe in hexane at −78 °C produced the μ-oxo methyl complex **4**, which was isolated as a yellow solid in good yield. Compound **4** is thermally stable and can be stored under inert conditions without appreciable decomposition, although in air it spontaneously evolves, probably through further hydrolysis reactions of the Ti−Me bonds. A rapid exploration on the reactivity of the methylene titanium species shows its ability for the methylenation of carbonyl compounds. Complex **3** reacts slowly with benzophenone, at 90 °C in C_6D_6, to afford the olefin $Ph_2C{=}CH_2$ and the μ-oxo titanium complex **4**, as indicated by NMR spectroscopy. The reactivity observed between **3** and benzophenone follows well-established "Wittig-type" reagents studied in organic synthesis (Scheme 1).

The ^1H NMR spectra (C_6D_6 at room temperature) of compounds **3** and **4** show four and two signals for the methyl-cyclopentadienyl and methyl-silyl protons, respectively. The Ti−Me protons appear as a singlet, while the μ-methylene group resonance, for compound **3**, is observed as a singlet at δ 5.90. Similar spectroscopic features are observed in the ^{13}C NMR spectra, with the more remarkable resonance assignable to the methylene carbon atom, which gives rise to a triplet at δ 196.9 with a coupling constant value $^2J_{H-H} = 118.8$ Hz. In accordance with their ^1H and ^{13}C spectra, we propose both complexes to have a folded structure held by the bridging unit, either a methylene or oxo functionality. For both complexes, the ^1H and ^{13}C spectra exhibit peaks for the ancillary ligand as expected for C_2-symmetric compounds, which contrasts with the average C_{2h} symmetry of complexes **1** and **2**. As a result, the distal and proximal methyl groups of the cyclopentadienyl ligand and the methyl groups bonded to silicon are not equivalent, showing pairs of resonances, whereas the Ti−Me ligand appears as a unique signal. Additionally, in the case of **3**, a diagnostic of the bridging methylene unit are the low field shifts for both the protons and carbon nuclei of the methylene group.

Single-crystal X-ray diffraction (Figure 1) confirmed the presence of the μ-methylene moiety and revealed the folded structure of **3**. The molecular structure shows a dinuclear species with both metallic moieties symmetry related by a 2-fold axis perpendicular to the Ti···Ti^i (i: $-x$, $+y$, $-z + 1/2$) distance and passing through the bridging methylene carbon atom. In the molecule, two "$Ti(C_5Me_4SiMe_2)Me$" units are connected by two oxygen bridges (Ti−O−Si) and a symmetrical μ-CH_2 bridge (Ti−CH_2−Ti^i). The Ti−C(1)−Ti^i angle

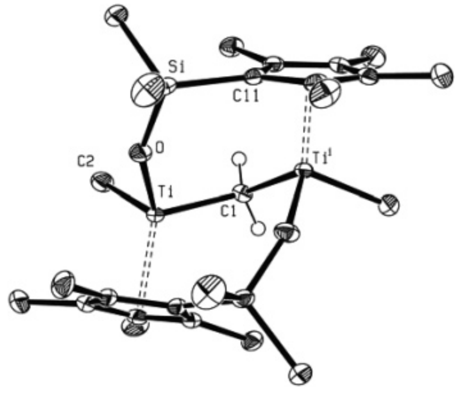
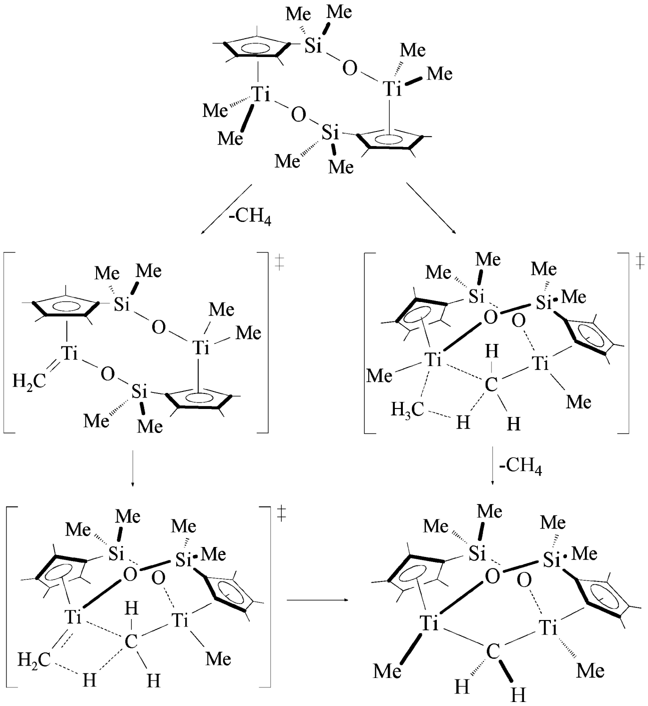


Figure 1. Thermal ellipsoid plot of **3** (50% probability). Selected bond lengths (Å) and angles (deg): Ti−O 1.8270(11), Ti−C(1) 2.0719(13), Ti−C(2) 2.1215(17), Ti···Ti^i 3.3708(5), Si−O 1.6404(12), Si−C(11)^i 1.8735(16), O−Ti−C(1) 103.03(5), O−Ti−C(2) 101.28(6), C(1)−Ti−C(2) 101.09(7), Ti−C(1)−Ti^i 108.87(10). Symmetry transformation used to generate equivalent atoms: i $-x, y, -z + 1/2$.

Scheme 2



[108.87(10)°] is close to the ideal value for an sp^3-hybridized carbon atom and significantly larger than those found in heterodinuclear Ti-methylidene complexes.[3] The Ti−C(1) distance [2.0719(13) Å] is slightly shorter than the Ti−C(2) distance [2.1215(17) Å] and compares well with those reported for related dinuclear compounds.[6] Both the Ti−C(1)−Ti^i angle and the long Ti···Ti^i distance [3.3708(5) Å] infer the absence of a metal−metal interaction.

The formation of μ-methylene species is associated with olefin polymerization catalyst deactivation.[9,11] Although no intermediates have been observed, the two most likely pathways for the formation of **3** are *intra*- or *inter*metallic α-H abstraction[12] (Scheme 2). α-Hydrogen abstraction by the *geminal* titanium-methyl group must give the terminal methylene intermediate [{(Ti=CH$_2$)(TiMe$_2$)[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]$_2$}], which subsequently undergoes *vicinal* titanium-methyl C−H addition across the Ti=C bond. An alternative pathway involves a direct σ-bond metathesis, in which the leaving methyl group comes from the adjacent titanium atom. In both cases, the key feature of **2** that enables this process is the flexibility of the central core "{Ti[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]}$_2$" which allows both titanium atoms to act cooperatively during the course of the process.

In conclusion, the results of this study show that the stable μ-methylene complex {Ti[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]Me}$_2$(μ-CH$_2$) is readily accessible from the tetramethyl derivative {Ti[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]Me$_2$}$_2$ under mild conditions by α-hydrogen abstraction. To the best of our knowledge, complex **3** constitutes the first example of a cyclopentadienyltitanium compound supporting a μ-methylene unit to be fully characterized by single-crystal X-ray diffraction. This μ-CH$_2$ derivative is spontaneously hydrolyzed, in solution, in the presence of traces of water to afford the isoelectronic μ-oxo {Ti[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]Me}$_2$(μ-O) compound and reacts with benzophenone following the typical "Wittig-type" reactions studied in organic chemistry.

Experimental Section

General Considerations. All manipulations were performed under argon using Schlenk and high-vacuum line techniques or in a glovebox, model HE-63. The solvents were purified by distillation under argon before use by employing the appropriate drying/deoxygenating agent. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. MgClMe (THF solution) (Aldrich) was commercially obtained and used without further purification. {Ti[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]Me$_2$}$_2$[10] and {Ti[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]Cl}$_2$(μ-O)[10] were prepared by known procedures. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. NMR spectra, measured at 25 °C, were recorded on a Varian Unity FT-300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75 MHz) or FT-500 (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz) spectrometer, and chemical shifts are referenced to SiMe$_4$ via the carbon resonances (^{13}C) and the residual protons (^{1}H) in the solvent.

Synthesis of {Ti[μ-(η5-C$_5$Me$_4$SiMe$_2$-O)]Me}$_2$(μ-CH$_2$) (3). A solution of {Ti[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]Me$_2$}$_2$ (0.30 g, 0.55 mmol) in toluene (15 mL) was stirred at 80 °C for 17 h. Concentration of the resulting yellow solution to ca. 5 mL and cooling to −20 °C gave **3** as a yellow crystalline solid (0.18 g, 62.00% yield). Anal. Calcd for C$_{25}$H$_{44}$O$_2$Si$_2$Ti$_2$: C, 56.8; H, 8.4. Found: C, 56.8; H, 8.6. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 0.49, 0.62 (s, 6H, SiMe); 0.73 (s, 6H, TiMe); 1.37, 1.83, 1.94, 2.77 (s, 6H, C$_5$Me$_4$); 5.90 (s, 2H, μ-CH$_2$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C): δ 4.5, 5.2 (SiMe); 12.1, 12.2, 15.0, 17.6 (C$_5$*Me*$_4$); 46.7 (q, J = 124 Hz, TiMe); 121.2, 124.2, 127.1 (*C*$_5$-Me$_4$); 196.9 (t, J = 118.8 Hz, μ-CH$_2$); two signals of *C*$_5$Me$_4$ are obscured by C$_6$D$_6$ signals.

Synthesis of {Ti[μ-(η5-C$_5$Me$_4$SiMe$_2$-O)]Me}$_2$(μ-O) (4). A 1.17 mL portion of a 3 M THF solution of MgClMe (3.5 mmol) was added at −78 °C to a suspension of {Ti[μ-(η^5-C$_5$Me$_4$SiMe$_2$-O)]Cl}$_2$(μ-O) (1 g, 1.75 mmol) in hexane (50 mL). The cooling bath was removed, and the reaction mixture was slowly warmed to room temperature and stirred for 3 h. After filtration the solvent was evaporated under vacuum and the resulting residue was extracted into hexane (25 mL). The solution was concentrated and cooled to −20 °C to give a yellow solid. Recrystallization with hexane/toluene gave compound **4** as a microcrystalline yellow product (0.50 g, 54.00% yield). Anal. Calcd for C$_{24}$H$_{42}$O$_3$Si$_2$Ti$_2$: C, 54.3; H, 7.9. Found: C, 53.9; H, 7.8. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 0.51, 0.57 (s, 6H, SiMe); 0.85 (s, 6H, TiMe); 1.80, 1.94, 2.10, 2.29 (s, 6H, C$_5$Me$_4$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C): δ 4.0, 5.3 (SiMe); 11.4, 11.8, 15.1, 15.4 (C$_5$*Me*$_4$); 43.6 (TiMe); 120.9, (C$_{ipso}$-C$_5$Me$_4$); 127.8, 127.4,130.5, (*C*$_5$Me$_4$); one signal of *C*$_5$Me$_4$ is obscured by C$_6$D$_6$ signals.

X-ray Structure Determination of {Ti[μ-(η5-C$_5$Me$_4$SiMe$_2$-O)]Me}$_2$(μ-CH$_2$) (3). Crystals of **3** suitable for X-ray diffraction studies were obtained by recrystallization from toluene/hexane. An ORTEP drawing of **3** showing the numbering scheme used in the refinements is illustrated in Figure 1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-230788 Additional crystallographic data are available in the Supporting Information.

3: yellow prism of 0.45 × 0.25 × 0.23 mm size, grown from toluene at −20 °C, C$_{25}$H$_{44}$O$_2$Si$_2$Ti$_2$, M = 528.58, monoclinic, space group *C*2/*c*, a = 19.3362(6) Å, b = 8.6521(3) Å, c =

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18.9018(6) Å, $\beta = 119.89°$, $V = 2741.7(2)$ Å^3, $Z = 4$, $D_c = 1.281$ gcm^{-3}, $\theta_{max} = 29.0°$, diffractometer Bruker SMART APEX CCD, Mo Kα ($\lambda = 0.71073$ Å), ω-scan, $T = 100(2)$ K, $\mu = 0.689$ mm^{-1}, 20 833 reflections collected, 3468 independent ($R_{int} = 0.0164$), reflections corrected for absorption (multiscan, SADABS, T_{min}/T_{max} 0.821), direct primary solution and refinement on F^2 (SHELXL-97, G. M. Sheldrick, University of Göttingen, 1997), 148 refined parameters, rigid methyl group hydrogen atoms, other riding, $\Delta\rho$ (e·Å^{-3}) = 0.42, $R_1[I > 2\sigma(I)] = 0.0335$, wR_2(all reflections) = 0.0859.

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Supporting Information Available: X-ray crystallographic data for the structure of **3** are available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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