The Elusive Titanocene

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Although bis-cyclopentadienyl derivatives of the group 4 transition metals have been proposed as reactive intermediates in a wide range of reactions, none have been structurally characterized. Attempts to prepare Ti(η-Cp)$_2$ have been frustrated by the reactivity associated with this carbene analogue. To date, all structurally characterized titanocenes have required the coordination of neutral ligands such as N_2, CO, pyridine, phosphines, or acetylenes in order to stabilize the d^2 metallocene moiety. Moreover, all of these derivatives exhibit nonparallel cyclopentadienyl rings (Table 1).[1−9] More recently, our colleagues at Sussex have prepared and structurally characterized the bent metallocene, Ti(η-C$_2$P$_3$Bu$^t{}_2$)$_2$.[10] We now report the synthesis of Ti(η^1-Cp^s)$_2$Cl (**1**) and [Ti(η-Cp^s)$_2$] (**2**) (Cp^s = C$_5$Me$_4$(SiMe$_2$Bu^t)) and in the case of the latter the first example of a structurally authenticated titanocene. Furthermore, due to the steric demand of the Cp^s ligands, a parallel configuration for the Cp^s ligands is observed.

Table 1. Selected Structural Data for Selected Titanocenes

cmpd	M$_1$−Ti−M$_2$ angle (deg)	Ti−M distance (Å)
[{Ti(η-C$_5$HMe$_4$)(μ−η^2:η^5-C$_5$Me$_4$)}$_2$][1]	141	2.0515(9), 2.0231(9)
Ti(η^5-C$_5$Me$_5$)$_2$[η^2-{C(SnMe$_3$)}$_2$][2]	141	2.115(14)
Ti(η^5-C$_5$Me$_5$)$_2$[η^2-{C(SiMe$_3$)}$_2$][3]	139	2.118, 2.109
Ti(η^5-C$_5$H$_5$)$_2$[η^2-{C(SiMe$_3$)CPh}][3]	139	2.115−2.117(14)
[Ti(η^5-C$_5$Me$_5$)$_2$(μ-N$_2$)][4]	145−146	2.061−2.071
[Ti(η^5-C$_5$Me$_5$)$_2$(η^2-C$_2$H$_4$)][5]	144	2.092(5)
[Ti(η^5-C$_5$Me$_5$)$_2$(CO)$_2$][6]	148	2.06, 2.07
[Ti(η^5-C$_5$H$_5$)$_2$(PF$_3$)$_2$][7]	137, 138	2.012−2.020
[Ti(η^5-C$_5$H$_4$Me)$_2$dmpe][8]	135	2.039, 2.052
[Ti(η^5-C$_5$H$_5$)$_2$(PMe$_3$)$_2$][9]	133, 134	2.049−2.062(14)
[Ti(η^5-Cp^s)$_2$]	180	2.018(4)
[Ti(η^5-Cp^s)Cl$_3$][18]		2.027

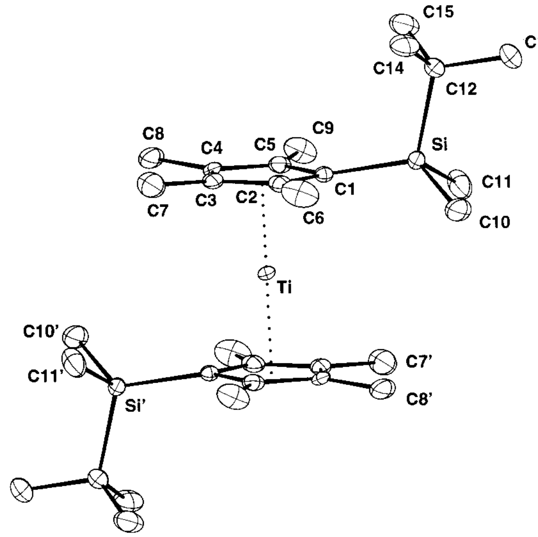

Figure 1. The molecular structure of **2** and atom numbering scheme with selected bond lengths (Å) and angles (deg): Ti−M(1) 2.018(4), Ti(1)−C(1) 2.315(3), Ti−C(2) 2.341(3), Ti−C(3) 2.386(4), Ti−C(4) 2.383(4), Ti−C(5) 2.334(3), M(1)−Ti-M(1′) 180.0. M(1) denotes the centroid of the ring C(1) to C(5).

The reaction of 2 equiv of the lithium salt of Cp^s with TiCl$_3$ in hexanes/THF afforded Ti(η^5-Cp^s)$_2$Cl. Recrystallization from toluene produced green crystals in high yield (74%).[11] The reduction of **1** using Na/Hg amalgam resulted in the isolation of **2** as a red-brown solid which was subsequently recrystallized from toluene.[12] The molecular structure of **2** was determined.[13] The Ti atom sits on an inversion center between equidistant cyclopentadienyl rings that are planar, staggered, and exactly parallel (Figure 1). The SiMe$_2$Bu^t substituents are rotated by 180° with respect to one another, with the Me groups directed toward and the Bu^t group away from the Ti. The Ti-centroid distance, 2.018(4) Å, is relatively short compared with those previously measured for other metallocenes of Ti^{II} and is similar to that observed in a related Ti(IV) derivative (Table 1). As in the case of [Fe(η^5-Cp^s)$_2$], [Sn(η^5-Cp^s)$_2$],[14] and [Pb(η^5-Cp^s)$_2$],[15] the steric

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(11) Synthesis of Ti(η^5-Cp^s)$_2$Cl. To a Schlenk tube charged with a slurry of TiCl$_3$•3THF (1.53 g, 4.13 mmol) in hexanes/THF (80:20, 50 mL) cooled to 0 °C by using an ice bath was added over a 2 min period with stirring a slurry of LiC$_5$Me$_4$(SiMe$_2$Bu^t) (2.00 g, 8.26 mmol) in hexanes (40 mL) at 0 °C. Stirring was continued for 0.5 h, after which the mixture was allowed to warm to ambient temperature. After the solution was stirred for a further 18 h, Ti{η-C$_5$Me$_4$(SiMe$_2$Bu^t)}$_2$Cl was obtained as a green, O$_2$- and H$_2$O-sensitive powder by filtration of the solution and removal of the solvent in vacuo. Yield 74% (1.70 g, 3.07 mmol). Recrystallisation from toluene at ca. −28 °C afforded dark green cubes. Mp 189.5 °C. ^{1}H NMR (C$_6$D$_6$, 400.13 MHz, 303K): δ 1.80 [br], 2.44 [br], 3.27 [br]; EI MS: M$^{+\bullet}$ *m/z* 553 (100%), M$^{+\bullet}$ −Cl *m/z* 518 (7%), M$^{+\bullet}$ −Bu^t *m/z* 496 (96%), [C$_5$Me$_4$(SiMe$_2$Bu^t)]$^+$ −Bu^t *m/z* 177 (43%), [SiMe$_3$]$^{+\bullet}$ *m/z* 73 (84%). Elemental analysis for C$_{30}$H$_{54}$Si$_2$TiCl: C, 65.01 (64.33); H, 9.82 (9.39).

(12) Synthesis of [Ti(η^5-Cp^s)$_2$]. To a Schlenk tube charged with Ti{η-C$_5$Me$_4$(SiMe$_2$Bu^t)}$_2$Cl (1.08 g, 1.95 mmol) in toluene (100 mL) was added with stirring, sodium amalgam (116 g, 0.4% w/w). The mixture was stirred for 72 h and filtered through a 5-cm Celite column. [Ti{η-C$_5$Me$_4$(SiMe$_2$Bu^t)}$_2$] was obtained as a brown, moderately O$_2$- and H$_2$O-sensitive powder by removal of the toluene in vacuo. Yield 89% (0.90 g, 1.74 mmol). Recrystallisation from toluene at ca. −28 °C afforded dark red cubes. Mp ca. >195 °C (decomp). ^{1}H NMR (C$_6$D$_6$, 400.13 MHz, 298K): δ 2.02 [br, s, 6H], 6.67 [s, 9H], 23.90 [br, s, 6H], 81.15 [br, s, 6H]; EI MS: M$^{+\bullet}$ *m/z* 518 (3%), M$^{+\bullet}$ −[C$_5$Me$_4$(SiMe$_2$Bu^t)] *m/z* 281 (55%), [C$_5$Me$_4$(SiMe$_2$Bu^t)]$^{+\bullet}$ *m/z* 236 (76%), [C$_5$Me$_4$(SiMe$_2$Bu^t)]$^{+\bullet}$ −Bu^t *m/z* 177 (78%), [SiMe$_3$]$^{+\bullet}$ *m/z* 73 (100%). Elemental analysis for C$_{30}$H$_{54}$Si$_2$Ti: C, 69.45 (68.81); H, 10.49 (10.32). λ_{max} = 569 nm, ϵ = 52 mol^{-1} cm^{-1}. μ_{Eff} = 2.4 μ_B; Evan's method.

(13) Crystal data for [Ti{η-C$_5$Me$_4$(SiMe$_2$Bu^t)}$_2$]. C$_{30}$H$_{54}$Si$_2$Ti. The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares procedure. For $T = 173(2)$ K, specimen 0.4 × 0.4 × 0.3 mm, $M = 518.8$, monoclinic, spacegroup $P2_1/n$ (No. 14), $a = 13.250(2)$, $b = 8.5032(7)$, $c = 13.807(1)$ Å, $\beta = 93.566(8)$, $V = 1553(1)$ Å^3, $D_{calc} = 1.11$ g cm^{-3}, $Z = 2$. For reflections with $2 \le \theta \le 25$, R1(F) = 0.058 for 2147 observed reflections [$I > 2\sigma(I)$] and wR2(F^2) = 0.161 for all 2845 reflections.

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demands of the Cp^s ligands result in a parallel configuration of the Cp^s rings rather than the "bent" structure anticipated from electronic considerations. Both extended Hückel calculations[16] and, more recently, ADF-based results[17] have shown that for a d^2 metallocene there is no significant change in energy as the metallocene bends (ca. 40°), unlike for ferrocene where deviations from a parallel configuration result in a significant increase in energy. We propose that the parallel nature of the cyclopentadienyl rings of **2** is due to the methyl−methyl repulsions which would arise from any further decrease in the C(7)−C(11′), C(7′)-C(11) and the C(8)−C(10′), C(8′)-C(10) distances, 3.553(5) and 3.475(5) Å, respectively. Furthermore, the energy required to bend the $SiMe_2{}^tBu$ out of the cyclopentadienyl plane, as observed in the case of $[Fe(\eta^5\text{-}Cp^s)_2]$ (16.6°),[14] would not be compensated for by a concomitant decrease in energy obtained upon bending. Additionally, a lateral displacement of the Cp^s rings with respect to one another is also evident from the short Ti−C(1) bond. Solid samples of **2** are remarkably stable with respect to aerial oxidation (decomposing on standing overnight) although solutions turn bright yellow immediately upon exposure to air. The ^1H NMR spectra of **1** and **2** each displayed broad resonances characteristic of paramagnetic species. For **2**, a determination of the magnetic moment was undertaken ($\mu = 2.4$) and was consistent with the $(e_{2g})^2$ nature of the ground state.

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Supporting Information Available: Structure determination summary, tables of isotropic and anisotropic displacement parameters, tabulation of bond lengths and bond angles (7 pages, print/PDF). An X-ray crystallographic file in CIF format is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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