The Ti(IV) Complex of a Benzannulated N-Heterocyclic Carbene

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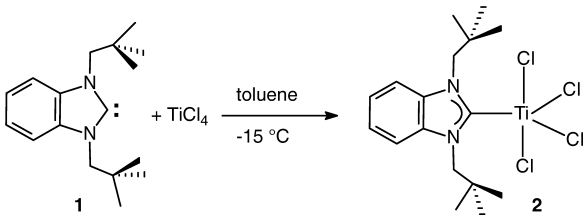
The yellow titanium(IV) carbene complex [$TiCl_4$(**1**)], **2** (**1** = *N,N'*-bis(2,2-dimethylpropyl)benzimidazol-2-ylidene) was synthesized by reaction of $TiCl_4$ and the benzannulated carbene **1** in toluene. The X-ray structure analysis revealed a mononuclear complex with a titanium(IV) center coordinated in a distorted trigonal-bipyramidal fashion by the carbene ligand in an equatorial position and four chloro ligands.

Key words: Carbene Ligand, Titanium(IV), Crystal Structure

Introduction

Stable N-heterocyclic carbenes have found widespread applications in coordination chemistry and catalysis [1]. They have been employed as ligands in the organometallic chemistry of elements from all parts of the Periodic Table. Surprisingly, only few examples of group 4 metal complexes with N-heterocyclic carbene ligands have been described so far. In 1994 Herrmann et al. prepared a series of [(1,3-dimethylimidazol-2-ylidene)$_2$MCl$_4$] complexes (M = Ti, Zr, Hf) [2]. Kuhn *et al.* reported in 1995 the molecular structure of the dinuclear μ-oxo-bridged complex [(L)TiCl$_3$(μ-O)TiCl$_3$(L)] (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) obtained by the reaction of $TiCl_4$ and the carbene ligand followed by careful hydrolysis [3]. A titanium(IV) complex containing a chelating biscarbene ligand has been described [4] and cationic complexes of the type [(C$_5$H$_5$)$_2$Ti(CH$_3$)(L)]$^+$ (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) are known [5]. We attempted to prepare Ti(IV) complexes with N-heterocyclic carbenes from $TiCl_4$ and β-functionalized phenyl isocyanides [6] by intramolecular nucleophilic cyclization [7], but were unsuccessful. We describe here the reaction of the stable benzannulated N-heterocyclic carbene **1** [8] with $TiCl_4$ yielding the pentacoordinated carbene complex **2** (Scheme 1).



Scheme. 1. Synthesis of complex **2**.

Experimental Section

All manipulations were performed in an atmosphere of dry argon by standard Schlenk techniques. Solvents were dried by standard methods und freshly distilled prior to use. *N,N'*-bis(2,2-dimethylpropyl)benzimidazol-2-ylidene **1** was prepared according to a published procedure [8a].

*[TiCl$_4$(N,N'-bis(2,2-dimethylpropyl)benzimidazol–2–ylidene)] **2***: A solution of 258 mg (1 mmol) of **1** in 40 ml of toluene was treated dropwise with 0.9 mmol of freshly distilled titanium(IV) chloride at -15 °C. Upon addition of the $TiCl_4$ the reaction mixture turned immediately brownish. After stirring for 30 minutes the solution was filtered and the solvent was removed under reduced pressure. Yellow crystals, suitable for an X-ray diffraction analysis, were obtained from a concentrated toluene solution at 0 °C. Yield: 251 mg (0.56 mmol, 62%). ^{1}H NMR (600 MHz, [D$_8$]toluene, ppm): $\delta = 7.04 - 7.02$ (m, 2 H, Ar-H), 6.92 – 6.90 (m, 2 H, Ar-H), 4.03 (s, 4 H, NCH$_2$), 0.88 (s, 18 H, CH$_3$). – ^{13}C NMR (50.3 MHz, [D$_8$]toluene, ppm): $\delta = 196.0$ (Ti-C), 133.7 (Ar-C), 124.2 (Ar-C), 113.8 (Ar-C), 59.4 (NCH$_2$), 34.5 (*C*-(CH$_3$)$_3$), 29.7 (CH$_3$).

X-ray structure determination: Formula C$_{17}$H$_{26}$N$_2$Cl$_4$Ti, $M = 448.1$, yellow crystal $0.25 \times 0.15 \times 0.15$ mm^3, $a = 14.130(1)$, $b = 9.534(1)$, $c = 15.786(1)$ Å, $\beta = 94.65(1)^\circ$, $V = 2119.6(3)$ Å^3, $\rho_{calcd} = 1.404$ g cm^{-3}, $\mu = 9.10$ cm^{-1}, empirical absorption correction ($0.804 \leq T \leq 0.876$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 12808 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 4840 independent ($R_{int} = 0.044$) and 3242 observed reflections [$I \geq 2\sigma(I)$], 223 refined parameters, $R = 0.042$, $wR2 = 0.081$, max. residual electron density 0.32 (-0.34) e Å^{-3}, hydrogen atoms on calculated positions and refined as riding atoms. The data

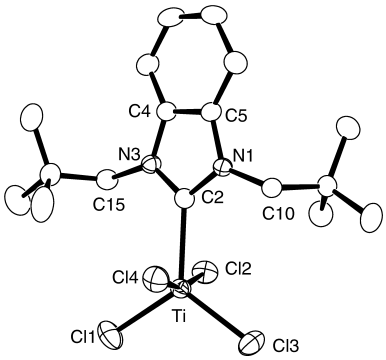


Fig. 1. Molecular structure of complex [$TiCl_4$(**1**)] **2**. Hydrogen atoms have been omitted. Selected bond lengths [Å] und angles [°]: Ti-C2 2.221(2), Ti-Cl1 2.1902(8), Ti-Cl2 2.2611(8), Ti-Cl3 2.2087(8), Ti-Cl4 2.2638(8), N1-C2 1.357(3), N1-C5 1.391(3), N1-C10 1.473(3), N3-C2 1.352(3), N3-C4 1.390(3), N3-C15 1.473(3); C2-Ti-Cl1 125.50(6), C2-Ti-Cl2 81.91(6), C2-Ti-Cl3 123.65(6), C2-Ti-Cl4 81.83(6), Cl1-Ti-Cl2 94.24(3), Cl1-Ti-Cl3 110.84(3), Cl1-Ti-Cl4 96.00(3), Cl2-Ti-Cl3 94.03(3), Cl2-Ti-Cl4 163.72(3), Cl3-Ti-Cl4 94.13(3), Ti-C2-N1 125.9(2), Ti-C2-N3 127.7(2), N1-C2-N3 106.4(2).

set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT [9], data reduction Denzo-SMN [10], absorption correction SORTAV [11], structure solution SHELXS-97 [12], structure refinement SHELXL-97 [13], graphics ORTEP [14]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 229648. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

The reaction of titanium(IV) chloride with one equivalent of the benzannulated carbene **1** yields the carbene complex **2** as a yellow solid. Only one carbene ligand is coordinated to the metal center. The reaction of two equivalents of **1** with $TiCl_4$ yields also only complex **2**. We assume, that the bulky N-substituents of carbene **1** prevent the coordination of two carbene ligands to $TiCl_4$. The existence of mono and dicarbene complexes of $TiCl_4$ has been predicted [15] and was observed with sterically less bulky substituted N-heterocyclic carbenes depending on the stoichiometry [2, 3]. Complex **2** is air-sensitive and becomes hydrolyzed to white titanium dioxide upon contact with air.

The X-ray structure analysis reveals a strongly distorted trigonal-bipyramidal ($\tau = 0.64$ [16]) molecular geometry for **2** (Fig. 1). The titanium(IV) center is coordinated by one benzannulated carbene ligand and four terminal chloro ligands. The carbene ligand occupies an equatorial position in the distorted trigonal bipyramid. A similar behaviour was observed in [(L)$TiCl_3$(μ-O)$TiCl_3$(L)] (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) [3]. The Ti-C2 distance in **2** (2.221(2) Å) compares well with the Ti-C bond length in other Ti(VI) complexes with N-heterocyclic carbenes. As observed for [(L)$TiCl_3$(μ-O)$TiCl_3$(L)], the equatorial Ti-Cl bond lengths (Ti-Cl1 2.1902(8), Ti-Cl3 2.2087(8) Å) are slightly shortened in comparison with the axial ones (Ti-Cl2 2.2611(8), Ti-Cl4 2.2638(8) Å). The carbene carbon atom is in a planar (sum of angles around C2 360.0°) configuration.

Complex **2** is the first structurally characterized carbene adduct of $TiCl_4$ and only the second complex reported with the sterically demanding bis(neopentyl)-substituted benzannulated N-heterocyclic carbene ligand **1**.

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