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Synthesis and structure of isopropyldimethylsilyl-substituted octamethyltitanocene

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Abstract

Reduction of isopropyldimethylsilyl-substituted titanocene dichloride [$TiCl_2(\eta^5\text{-}C_5Me_4SiMe_2Pr^i)_2$] (**1**) by excess magnesium in the presence of excess bis(trimethylsilyl)ethyne (btmse) in tetrahydrofuran at 60 °C yielded a mixture of products amongst them only the trinuclear Ti–Mg–Ti hydrido-bridged complex $Mg[Ti(\mu\text{-}H)_2(\eta^5\text{-}C_5Me_4SiMe_2Pr^i)]_2$ (**3**) was isolated and characterized. The precursor of titanocene, $[Ti(\eta^5\text{-}C_5Me_4SiMe_2Pr^i)_2(\eta^2\text{-btmse})]$ (**6**), was obtained from the identical system which, after initial formation of $[TiCl(\eta^5\text{-}C_5Me_4SiMe_2Pr^i)_2]$ (**2**), reacted at −18 °C overnight and then the solution was rapidly separated from the remaining magnesium. Titanocene $[Ti(\eta^5\text{-}C_5Me_4SiMe_2Pr^i)_2]$ (**7**) was obtained by thermolysis of **6** at 75 °C in vacuum. Crystal structures of **1**, **2**, **3**, **6**, and **7** were determined.

Keywords: Titanium; Titanocene; Silyl substituent; Isopropyldimethylsilyl; Bis(trimethylsilyl)ethyne-titanocene thermolysis; NMR spectra; X-ray crystallography

1. Introduction

Thermally stable, well-defined crystalline titanocenes are known only a few, all of them containing triorganylsilyl group in addition to four methyl groups on each of the two cyclopentadienyl ligands [1–3]. The titanocene containing *tert*-butyldimethylsilyl group was obtained from the appropriate titanocene monochloride by the reduction with sodium amalgam [1], that one containing trimethylsilyl group by thermolysis of its bis(trimethylsilyl)ethyne (btmse) complex [2], and the titanocenes containing phenethyldimethylsilyl and methyldiphenylsilyl groups were prepared by a direct reduction of the particular titanocene dichloride by magnesium in tetrahydrofuran (thf) [3] (Chart 1). Decamethyltitanocene [4] seems to be further stabilized by the replacement of one methyl group on each cyclopentadienyl ligand by a more bulky group, like *iso*-propyl or *tert*-butyl [5]. Although none of these solely carbonaceous titanocenes has been crystallographically characterized the crystal structures of their nitrogen complexes $[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)]$ [6] and $[Ti(\eta^5\text{-}C_5Me_4Pr^i)_2(\eta^1\text{-}N_2)_2]$ were determined [5]. The stability of titanocenes $[Ti(\eta^5\text{-}C_5Me_4R)_2]$ and their nitrogen complexes follow opposite trends. The thermal stability of the nitrogen complexes was found to be decreasing in the order of R: $Me > Pr^i > SiMe_3 > Bu^t$ [5], and for the titanocenes it is only known that the titanocene for $R = SiMe_3$ is stable at 70 °C [2] whereas that for R = Me forms an equilibrium with its hydride at room temperature [4]. A similar trend applies also to titanocene–btmse complexes. The $[Ti(\eta^5\text{-}C_5Me_4R)_2(\eta^2\text{-btmse})]$ complex for R = Me thermolyzes at 150 °C to give the double tucked-in (allyl-diene) titanocene $[Ti\{\eta^5\text{-}C_5Me_3(CH_2)_2\}(\eta^5\text{-}C_5Me_5)]$ [7] whereas for $R = SiMe_3$ it eliminates smoothly btmse to give the titanocene

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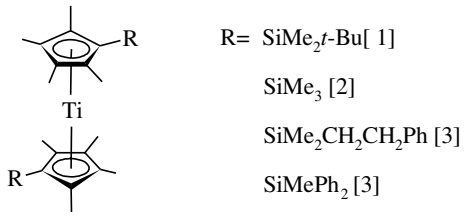


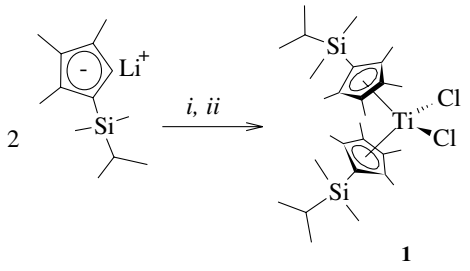
Chart 1.

at only 80 °C [2]. On the other hand, the titanocene for $R = SiMePh_2$ coordinates btmse reluctantly forming an observable equilibrium concentration of the adduct only at a large excess of free btmse [3], and neither the titanocene nor its btmse complex was found for $R = SiMe_2(CH_2CH_2CF_3)$ [8].

In this work, we investigate the preparation of the titanocene for $R = SiMe_2Pr^i$ attempting a direct reduction by magnesium as well as the route via thermolysis of its btmse complex.

2. Results and discussion

The synthesis of 5-(isopropyldimethylsilyl)-1,2,3,4-tetramethylcyclopenta-1,3-diene (Cp′H) and the corresponding titanocene dichloride $[TiCl_2(\eta^5\text{-}C_5Me_4SiMe_2Pr^i)_2]$ (**1**) thereof followed in all respects the synthesis of the trimethylsilyl derivatives (Scheme 1) [9]. Both the compounds were characterized by ^1H and ^{13}C NMR, IR, and EI-MS spectra and compound **1** by X-ray diffraction analysis. The EI-MS spectra of the both compounds showed fragmentations with the loss of Pr^i and Me groups. Compound **1** did not exert its molecular ion but gave a fragment ion arising from the loss of one cyclopentadienyl ligand as a base peak. The IR spectra showed absorption bands typical for the $SiMe_2Pr^i$ group at 1247 (vs) and 881 (s) cm^{-1} and very strong bands at 815 and 830 cm^{-1} for Cp′H or 811 (vs), 825 (s), and 834 (s) cm^{-1} for **1**. These bands vary only slightly in all the other titanocene derivatives.



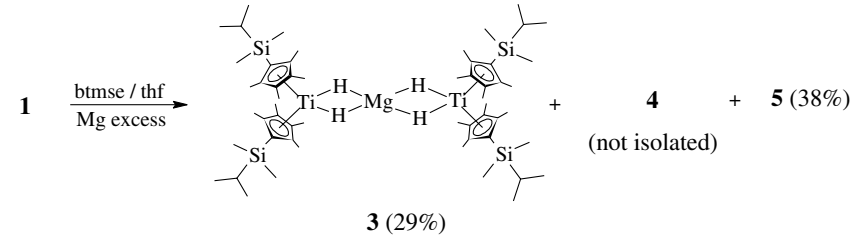
i $TiCl_3(thf)_3$, thf, boil for 20h.

ii 0.5 $PbCl_2$, workup

Scheme 1.

The reduction of **1** by a half molar equivalent of Mg rapidly afforded the blue, paramagnetic monochloride $[TiCl(\eta^5\text{-}C_5Me_4Pr^i)_2]$ (**2**) which displayed typical ESR and electronic absorption spectra common for highly methyl-substituted titanocene monochlorides [10,11]. The EI-MS spectra showed the molecular ion base peak which fragmentated with a loss of Me or Pr^i group. These fragments were then loosing the $SiMe_2Pr^i$ or the whole Cp′ ligand. Surprisingly, elimination of Cl or Cp′ from the molecular ion was not observed at all. The monomeric chemical formula of **2** was confirmed by X-ray crystal structure analysis (vide infra).

The clue complex for the thermolytic synthesis of titanocene, its btmse complex, could not be obtained by a standard procedure [7,12], i.e., the reduction of **1** with excess magnesium in thf in the presence of a 5-fold molar excess of btmse at 60 °C. Such a reaction resulted in the formation of a complex mixture of products (Scheme 2) from which the products low-soluble in hexane (**3**, **4**) and those contained in the mother liquor (**5**) were separated. The former products were dissolved in toluene and characterized by EPR spectra. The EPR spectra in solution and in the frozen glass indicated the presence of two titanocene–magnesium complex hydrides of known structural types. The trinuclear Ti–Mg–Ti hydrido complex $Mg[Ti(\mu\text{-}H)_2\{\eta^5\text{-}C_5Me_4(SiMe_2Pr^i)\}_2]_2$ (**3**) was easily recognized by EPR spectrum of the frozen glass showing an electronic triplet state of axial symmetry and its solid state structure was proved by X-ray diffraction analysis (vide infra). Compounds of the general formula $Mg[Ti(\mu\text{-}H)_2(\eta^5\text{-}Cp')_2]_2$ are known for $Cp' = C_5Me_5$ [13], C_5HMe_4, $C_5H_2Me_3$ [14], C_5Me_4Ph [15], and $C_5Me_4(SiMe_2CH_2CH_2CF_3)$ [8]. For this type of compounds the magnitude of the zero-field splitting D spans a narrow range of values ($D_{max} = 0.0133\ cm^{-1}$ for $Cp' = C_5HMe_4$ [14] and $D_{min} = 0.0116\ cm^{-1}$ for $Cp' = C_5Me_4(SiMe_2CH_2CH_2CF_3)$ [8]) because the distance between the spin-unpaired electrons residing on the Ti(III) atoms varies within 0.2 Å only. The present value of $D = 0.0117\ cm^{-1}$ is close to that for the above mentioned



Scheme 2.