Journal of Organometallic Chemistry 631 (2001) 16–18

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and crystal structure of oxo-bridged binuclear titanium complex [{Ti(acac)$_2$Cl}{TiCp$_2$(Cl)}(μ-O)] and its catalytic reactions toward silation of aldehyde

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Received 13 November 2000; received in revised form 10 May 2001; accepted 15 May 2001

Abstract

Reaction of [Cp$_2$TiCl$_2$] with two equivalents of 2,4-pentanedione in the presence of one equivalent of NEt$_3$ in CH$_3$CN at room temperature yielded oxo-bridged binuclear titanium complex [{Ti(acac)$_2$Cl}{TiCp$_2$(Cl)}(μ-O)], which was characterized crystallographically and spectroscopically. Reaction mixture of oxo-bridged binuclear titanium complex and 2^nBuLi catalytically activate the mixture of phenylsilane and aldehyde to yield *O*-silation products at room temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxo-bridged binuclear titanium; Diffraction studies; *O*-Silation; Aldehyde

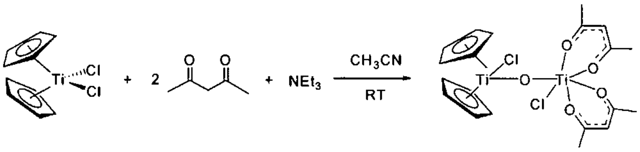
1. Introduction

Organometallic compounds of early transition elements have an important role in the development of both synthetic organometallic and catalytic chemistry [1,2]. Dialkyl metallocenes of Group 4 elements could be utilized as the catalysts for the hydrosilation of olefins and aldehydes, and dehydrogenative silation of alcohols [3]. During studies of the reactivity of 'Cp$_2$Ti(II)' [4] generated from [Cp$_2$TiCl$_2$] and 2^nBuLi toward diketones, we have reported the easy method for the preparation of [Ti(III)(acac)$_3$] complex [5] and titanocene(III) β-diketonate complexes [6], and their X-ray crystal structures [5,6]. We have also reported the alternative formation of [CpZr(acac)$_2$Cl], and its catalytic reaction toward various aldehydes [7].

In this report we wish to report the synthesis of oxygen-bridged titanium(IV) complex, [{Ti(acac)$_2$Cl}{TiCp$_2$(Cl)}(μ-O)] (**1**), and its catalytic reactions toward silation of aldehyde.

2. Results and discussion

Reaction of [Cp$_2$TiCl$_2$] with two equivalents of 2,4-pentanedione and one equivalent of NEt$_3$ in CH$_3$CN at room temperature resulted in the formation of a brownish red solution in 2 h (Eq. (1)). Layering of ether to the toluene extracts afforded red cubes of **1** in 40% yield. Complexities of the chemical shifts in ^{1}H-NMR spectrum of **1** in CDCl$_3$ prompted us to examine the diffraction studies of **1**. Fig. 1 shows a perspective view of **1** along with selected bond distances and angles.



(1)

A molecule consists of two titanium atoms, two chlorine atoms, two cyclopentadienyl, two acetylacetonate and an oxygen atom connecting the two titanium atoms. The distance of Ti(1)–O(5) in **1** is 1.914(3) Å and is 0.184(3) Å longer than the distance of Ti(2)–O(5). The distance between Ti(2) and oxygen

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PII: S0022-328X(01)01021-X

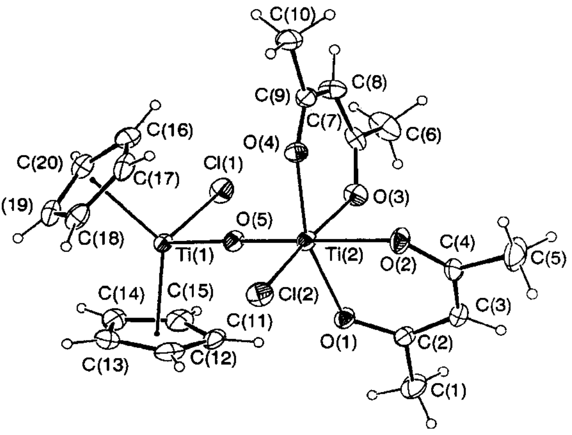

Fig. 1. ORTEP drawing of **1**. Selected bond distances (Å) and angles (°): Ti(1)–O(5) 1.914(3), Ti(2)–O(5) 1.730(3), Ti(2)–O(1) 1.980(4), Ti(2)–O(2) 2.105(4), Ti(2)–O(3) 2.010(4), Ti(2)–O(4) 1.982(4), Ti(1)–Cent(1) 2.052(3), Ti(1)–Cent(2) 2.058(3), Ti(1)–Cl(1) 2.3632(19), Ti(2)–Cl(2) 2.3405(19), Cl(1)–Ti(1)–O(5) 94.68(13), Cent(1)–Ti(1)–Cent(2) 131.63(14), Cl(2)–Ti(2)–O(5) 94.90(14). *Cent1: C(11), C(12), C(13), C(14), C(15). *Cent2: C(16), C(17), C(18), C(19), C(20).

ranges from 2.105(4) to 1.980(4) Å, with an average of 2.019(4) Å and is 0.05–0.06 Å longer than that of Ti–O in titanocene(III) β-diketonate complexes [5,6,8]. The five oxygen atoms and a chlorine Cl(2) atom coordinated Ti(2) atom form a slightly distorted octahedron. The O(5) atom bridges two titanium atoms almost linearly with an angle of 171.96(15)°.

It has been reported that [CpTi(acac)$_2$Cl] is prepared from the same reaction as Eq. (1), characterized spectroscopically, and ^{1}H-NMR spectrum of [CpTi(acac)$_2$Cl] reveals the co-existence of several isomers in solution state [9]. To find the source of the bridged oxygen, we examined the ^{1}H-NMR spectra of the crude products generated from the reaction of Eq. (1) in the presence of a stoichiometric amount of oxygen or water. ^{1}H-NMR spectrum of the crude materials reacted without oxygen or water was very similar to that of the products reacted in the presence of stoichiometric water or oxygen, respectively. Based on the results and Newton's work [9], the possibility of the formation of **1** from recombination of [CpTi(acac)$_2$Cl] during recrystallization could not be excluded. To identify the source of bridging oxygen, several experiments are now being undertaken.

Reaction of **1** with methyllithium, phenyllithium or a reducing reagent such as Na/Hg, K/Na or potassium naphthalenide resulted in the formation of intractable materials. However, a mixture of **1** and 2^{n}BuLi catalytically activated the mixture of phenylsilane and aldehyde to yield *O*-silation products at room temperature. When a mixture of propionaldehyde and phenylsilane was treated with a catalytic amount of **1** and 2^{n}BuLi in THF, tripropoxyphenylsilane was obtained as a yellow oil after flash chromatography, and characterized spectroscopically. Other aldehydes and phenylsilanes were similarly reacted with the catalytic amount of **1** and 2^{n}BuLi in THF (Eq. (2)), and the products were characterized by GC–MS. Results are summarized in Table 1.

$$\text{Aldehyde} + \text{PhSiH}_3 \xrightarrow[\text{THF}]{\mathbf{1} + 2^n\text{BuLi}} O\text{-silation products} \qquad (2)$$

For propionaldehyde and butyraldehyde, tris(alkoxy)phenylsilane was catalytically formed, respectively. However, a mixture of **1** and 2^{n}BuLi did not activate the acetaldehyde and the benzaldehyde. The reason for the failure of *O*-silation reaction was unclear, and efforts to elucidate the reasons and the pathway for *O*-silation reaction by **1** and ^{n}BuLi are being undertaken.

3. Experimental

3.1. General procedures

All manipulations were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. Acetonitrile was distilled from P$_2$O$_5$, and toluene and ether were distilled from potassium/benzophenone ketyl under nitrogen, respectively. All solvents were deoxygenated immediately prior to use. [Cp$_2$TiCl$_2$], 2,4-pentanedione, NEt$_3$, acetaldehyde, benzaldehyde, propionaldehyde, and butyraldehyde were purchased from Aldrich and used without purification. ^{1}H- and ^{13}C-NMR spectra were recorded at 25 °C on a Bruker AM 300 (^{1}H-NMR 300 MHz, ^{13}C-NMR 75.5 MHz) spectrometer and infrared spectra were obtained on a Shimadzu FTIR-8300. GC-MS were taken on a JEOL JES-DX 303 mass spectrometer equipped with JMA-DA 500 data system. X-ray diffraction studies were on crystals mounted on a fine glass rod. A minimum amount of epoxy resin was used to affix the crystal. X-ray data were collected on a Siemens R3m/V.

*3.2. Preparation of [{Ti(acac)$_2$Cl}{TiCp$_2$(Cl)}(μ-O)] (**1**)*

To a stirred solution of [Cp$_2$TiCl$_2$] (1.00 g, 4.0 mmol) in CH$_3$CN (ca. 60 ml) under nitrogen was added a solution of 2,4-pentanedione (0.83 ml, 8.0 mmol) and

Table 1
O-Silation products of aldehydes with phenylsilane catalyzed by **1** and 2^{n}BuLi

Aldehyde	Products	GC yield (%)
Acetaldehyde	–	No silation
Benzaldehyde	–	No silation
Propionaldehyde	(CH$_3$CH$_2$CH$_2$O)$_3$SiPh	53 [a]
Butyraldehyde	(CH$_3$CH$_2$CH$_2$CH$_2$O)$_3$SiPh	59 [b]

[a] Yield calculated after separation by flash chromatography.
[b] Yield calculated by GC–MS based on [aldehyde].

triethylamine (0.56 ml, 4.0 mmol) in CH_3CN (50 ml). The reaction mixture became brownish red, and stirring continued for 2 h at room temperature (r.t.). Volatile materials were removed under reduced pressure. The residues was taken up in toluene, 30 ml, and filtered, and the volume was reduced to ca. 10 ml. Layering of ether (40 ml) to a toluene solution gave **1** as rectangular cubes (0.82 g, 1.6 mmol, 40%); IR (Nujol mull) 3002 (w), 1600 (w), 1574 (w), 1525 (m), 1463 (vs), 1377 (m), 1352 (m), 1286 (w), 1269 (m), 1016 (vs), 930 (m), 826 (m), 798 (s), 785 (sh), 723(m), 665 (vs), 599 (m), 544 (m), 453 (s), 410 (w) cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.57–6.50 (m, 10H), 5.58 (m, 2H), 2.28–1.90 (m, 12H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 194.90, 191.67, 190.10, 185.24 (s, *C*O), 120.82, 119.62, 119.48, 119.03 (s, C_5H_5), δ 105.50, 105.00 (s, *C*H), δ 28.15, 27.02, 26.48, 25.84 (s, CH_3). Crystal data: monoclinic ($P21/c$) with $a = 13.4146(19)$, $b = 11.999(2)$, $c = 14.0801(16)$ Å, $\beta = 91.139(7)°$, $V = 2266.0(6)$ Å^3, $D_{calc} = 1.320$ Mg m^{-3}, $Z = 4$, $T = 22$ °C, $R_1 = 0.0508$ and $wR_2 = 0.1085$. Details are available in the supplementary material.

3.3. O-Silation reaction of aldehyde with phenylsilane catalyzed by 1 and ^{n}BuLi (aldehyde; propionaldehyde, butyraldehyde)

3.3.1. O-Silation reaction of propionaldehyde with phenylsilane catalyzed by 1

A solution of ^{n}BuLi (235 ml, 0.38 mmol, 1.6 M) in hexane was added to a solution of **1** (0.096 g, 0.19 mmol) in THF (5 ml) at −78 °C. The mixture was stirred for 10 min, and a solution of phenylsilane (2.51 ml, 20.3 mmol) and propionaldehyde (1.46 ml, 20.3 mmol) in THF (10 ml) was then added at 0 °C. The resultant mixture was stirred for 24 h at r.t. Flash chromatography (5% EtOAc in hexane) furnished [$(CH_3CH_2CH_2O)_3SiPh$] (1.02 g, 3.61 mmol, 53% yield) as a yellow liquid: IR (neat) 3072 (m), 3051 (m), 2936 (vs), 2876 (vs), 2735 (w), 1593 (w), 1464 (s), 1431 (s), 1391 (s), 1381 (m), 1304 (w), 1261 (m), 1084 (vs), 1016 (vs), 920 (m), 899 (m), 845 (vs), 797 (m), 735 (vs), 700 (vs) cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.77–7.40 (m, 5H), 3.84 (t, $J = 6.6$ Hz, 2H), δ 1.68 (m, 2H), δ 0.99 (t, $J = 7.4$ Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 134.70, 130.11, 127.64, 64.54, 25. 52, 10.08; GC–MS spectrum m/z 282 $[M]^+$.

3.3.2. O-Silation reaction of other butyraldehyde with phenylsilane catalyzed by 1

A solution of ^{n}BuLi (235 ml, 0.38 mmol, 1.6 M) in hexane was added to a solution of **1** (0.096 g, 0.19 mmol) in THF (5 ml) at −78 °C. The mixture was stirred for 10 min, and a solution of phenylsilane (2.51 ml, 20.3 mmol) and butyraldehyde (1.83 ml, 20.3 mmol) in THF (10 ml) was then added at 0 °C. The resultant mixture was stirred for 24 h at r.t. The resulting mixture was subjected to the GC–MS analysis after removing metal moieties by passing through Florisil, and the yield of $(CH_3CH_2CH_2CH_2O)_3SiPh$ was 59%, calculated by GC–MS based on the concentration of butyraldehyde. GC–MS (EI) Anal. Found: 324. Calc. for $C_{18}H_{32}O_3Si^+$: 324.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 151984 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support from the Korea Science and Engineering Foundation (971-0306-049-2) and Korea Research Foundation (2000–2001) are gratefully acknowledged.

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