

# $[(t\text{-Bu-DAD})\text{Ti}(\mu, \eta^2\text{-OCPh}_2)]_2\text{Mg}(\mu\text{-Cl})_2(\text{THF})$ : synthesis and molecular structure of a dimeric titanium ketone complex

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## Abstract

Reduction of  $[(t\text{-Bu-DAD})\text{TiCl}(\mu\text{-Cl})]_2$  (**1**) (*t*-Bu-DAD: *t*-BuN=CHCH=N*t*-Bu) with magnesium in the presence of benzophenone yields the  $\text{MgCl}_2$ -bridged dimeric titanium ketone complex  $[(t\text{-Bu-DAD})\text{Ti}(\mu, \eta^2\text{-OCPh}_2)]_2\text{Mg}(\mu\text{-Cl})_2(\text{THF})$  (**2**) whose molecular structure largely conforms with the assumptions about the structure of the first step of the reductive coupling of ketones at low-valent titanium. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Dimeric titanium ketone complex; Reductive coupling; Low-valent titanium

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The pinacol coupling reaction, which allows the generation of vicinal diols in one step, has been recognized as an important C–C bond forming process in synthetic organic chemistry [1]. Numerous methods exist that provide symmetrical diols via the homocoupling of aldehydes and ketones [2]. Nevertheless, despite the convenience of employing low-valent titanium or other transition metals as reducing agent in this reaction, the nature of the active species and intermediates in these carbonyl coupling reactions is not really known. It has often been proposed that the high stereoselectivity of benzaldehyde or acetophenone coupling is due to the formation of a binuclear complex binding both ketyl radicals, in which the aryl groups are arranged *anti* to each other to minimize steric interaction (Scheme 1, **a**) [3].

In other cases it is assumed that the coupling reaction relies on the formation of an  $\eta^2$ -carbonyl complex whose metal–carbon bond possesses sufficient nucleophilicity to attack another carbonyl compound (Scheme 1, **b**) [4,5]. In contrast to the radical reaction pathway this alternative mechanistic hypothesis implies a bielectronic reduction of the coordinated carbonyl compound.

In this paper, we describe first results of our work devoted to the search for low-valent titanium compounds stabilized by 1,4-diaza-1,3-diene (DAD) ligands which would be suitable for the synthesis of pinacols.

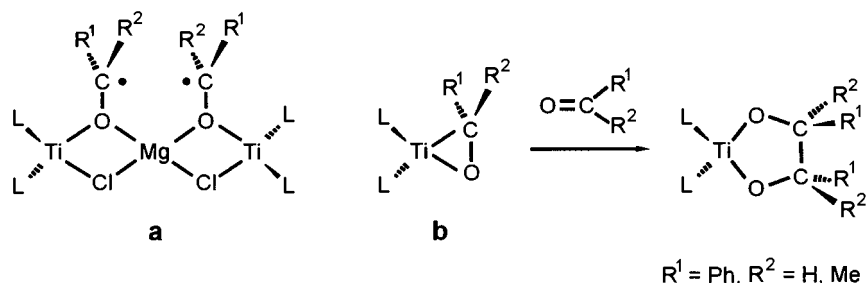
Some years ago Schobert had observed that  $\alpha, \beta$ -unsaturated aldehydes undergo a carbonyl coupling reaction when they react with “active titanocene” at low temperature [6]. Similarly to this way we found that pinacolate complexes  $\text{Cp}_2\text{Ti}[\text{OCPh}(\text{R})\text{CPh}(\text{R})\text{O}]$  (R = Me, Ph) are formed when  $\text{Cp}_2\text{TiCl}_2$  is reduced with Mg in the presence of acetophenone or benzophenone [7]. In an analogous manner we examined the reaction of  $[(t\text{-Bu-DAD})\text{TiCl}(\mu\text{-Cl})]_2$  (*t*-Bu-DAD: *t*-BuN=CHCH=N*t*-Bu) (**1**) [8] with Mg in THF in the presence of benzophenone. In the course of the reaction the solution became dark red and black-red crystals of complex **2** could be isolated in high yield (Scheme 2).

An X-ray structural study was performed to determine the precise molecular architecture of the product (Fig. 1). Complex **2** constitutes a trimetallic complex consisting of two  $[(t\text{-Bu-DAD})\text{Ti}]$  units bridged by a  $\text{MgCl}_2$  unit. In addition, each Ti atom is  $\eta^2$ -(O,C)-bonded to one molecule of benzophenone whose C–O bond lies perpendicular to the N–Ti–N plane of the  $[(t\text{-Bu-DAD})\text{Ti}]$  unit. Furthermore, the carbonyl O atoms are also coordinated to the central Mg atom. Therefore the coordination environment about this Mg

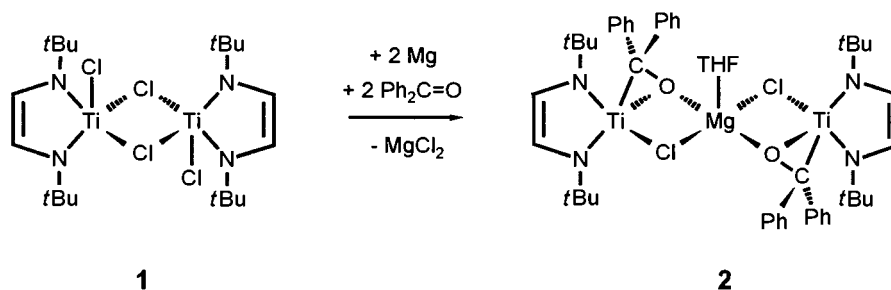
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Scheme 1. Formation of a diolate complex by: (a) coupling of two ketyl radicals within a dimeric titanium complex; or (b) by nucleophilic attack of an  $\eta^2$ -carbonyl complex to a further carbonyl compound.



Scheme 2. The generation of  $[(t\text{-Bu-DAD})\text{Ti}(\mu,\eta^2\text{-OCPh}_2)_2\text{Mg}(\mu\text{-Cl})_2(\text{THF})]$  (**2**).

atom is best described as a trigonal bipyramid in which the chlorine atoms Cl1 and Cl2 take the apical and the two carbonyl oxygen atoms O1 and O2 and the THF ligand the equatorial positions. The benzophenone C–O

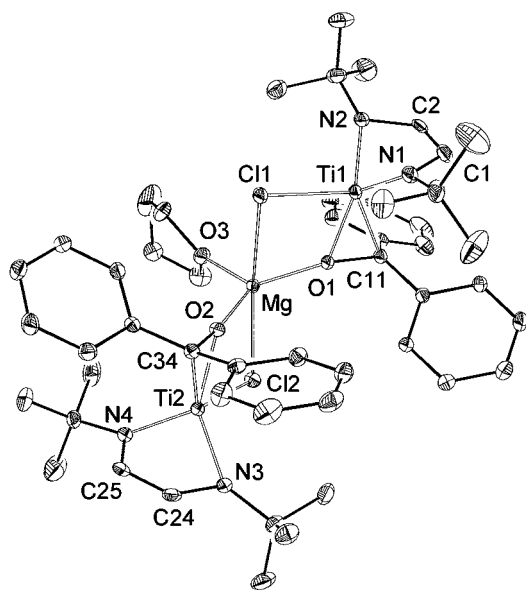


Fig. 1. Molecular structure of **2**. Selected bond length ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ti1–O1, 1.982(3); Ti2–O2, 1.978(3); Ti1–C11, 2.134(4); Ti2–C34, 2.117(4); Mg–O1, 1.924(3); Mg–O2, 1.924(3); Ti1–Cl1, 2.432(1); Ti2–Cl2, 2.446(1); Mg–O3, 2.016(3); O1–C11, 1.398(4); O2–C34, 1.389(4); Mg–Cl1, 2.526(2); Mg–Cl2, 2.505(2); Ti1–Cl1–O1, 64.4(2); Ti2–C34–O2, 64.9(2); C11–Ti1–O1, 39.5(1); C34–Ti2–O2, 39.5(1); Cl1–Mg–Cl2, 168.98(7).

distances of 1.398(4) (O1–C11) and 1.389(4)  $\text{\AA}$  (O2–C34) are comparable to those found in the  $\eta^2$ -benzophenone complexes  $[(2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O})_2\text{Ti}(\eta^2\text{-OCPh}_2)(\text{PMe}_3)]$  [9] or  $[\text{Cp}_2\text{Zr}(\eta^2\text{-OCPh}_2)(\text{THF})]$  [10] and to a certain extent also to those of the dimeric complex  $[\text{Cp}_2\text{Zr}(\eta^2\text{-OCPh}_2)]_2$  [11]. As expected they are substantially longer than the C=O double bond of free benzophenone [12] and together with the Ti–C and Ti–O distances, which have single-bond character, they indicate a bonding description involving a titanoxacyclopropane ring (Table 1).

Comparing the structure of **2** with that of the proposed intermediate for the diastereoselective coupling of aldehydes [2,3,13] (Scheme 1, a) it is striking that their overall molecular framework is surprisingly similar. The most remarkable difference concerns the configuration of the carbonyl compounds within the

Table 1  
Selected bond lengths ( $\text{\AA}$ ) of  $\eta^2$ -benzophenone complexes

	M–O	M–C	C–O	Ref.
$[(2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O})_2\text{-Ti}(\eta^2\text{-OCPh}_2)(\text{PMe}_3)]$	1.849(5)	2.150(7)	1.397(8)	[8]
$[\text{Cp}_2\text{Zr}(\eta^2\text{-OCPh}_2)(\text{THF})]$	2.041(3)	2.301(5)	1.389(5)	[9]
$[\text{Cp}_2\text{Zr}(\eta^2\text{-OCPh}_2)]_2$	2.109(2)	2.236(3)	1.425(4)	[10]
	2.112(2)	2.350(3)	1.419(4)	
<b>2</b>	1.982(3)	2.134(4)	1.398(4)	This work
	1.978(3)	2.117(4)	1.389(4)	
$\text{Ph}_2\text{CO}$			1.23	[11]

complex. In contrast to the proposed intermediate the two molecules of benzophenone in **2** are formally *trans* coordinated to the complex center without any sterical hindrance. Furthermore, in contrast to other  $\eta^2$ -ketone complexes [4,14] **2** does not react with an excess of benzophenone to yield a titanium diolate complex. Probably the increased stability of **2** caused by the Lewis acid  $\text{MgCl}_2$  is reflected by its lower reactivity. Viewed from this perspective, it seems questionable if the coupling of carbonyl compounds at low-valent titanium occurs via an intermediate with a structure similar to that of **2**.

## 1. Experimental

All reactions and manipulations were carried out using standard Schlenk techniques under an atmosphere of argon.

**Synthesis of 2:** To a violet solution of **1** (2.87 g, 5.0 mmol) in 50 ml THF at room temperature were added magnesium chips (0.243 g, 10.0 mmol) and benzophenone (1.82 g, 10.0 mmol). After stirring for 12 h the solvent was removed in vacuo and the dark red residue was extracted with 100 ml ether. Cooling the extract to  $-30^\circ\text{C}$  afforded black-red prisms of **2** (3.71 g, 77%). Crystals suitable for an X-ray analysis were obtained by recrystallization from ether at  $-30^\circ\text{C}$ . Correct elemental analysis.

**Spectroscopic data:**  $^1\text{H-NMR}$  (300 MHz,  $\text{THF-}d_8$ , 293 K):  $\delta$  7.43–6.25 (m, 20H, Ph), 6.00 (br s, 2H, HC=CH), 5.85 (br s, 2H, HC=CH), 3.61 (m, 2H,  $\text{OCH}_2\text{CH}_2$ , THF), 1.76 (m, 2H,  $\text{OCH}_2\text{CH}_2$ , THF), 0.92 (br s, 18H, *t*-Bu), 0.80 (br s, 18H, *t*-Bu).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{THF-}d_8$ , 293 K):  $\delta$  132.03 (TiCO), 146.28, 127.74, 124.72, 123.68 (Ph), 101.82 (NCH=), 67.40 (THF), 59.09 ( $\text{CMe}_3$ ), 30.54 ( $\text{CMe}_3$ ), 25.25 (THF).

**Crystal data for 2:**  $\text{C}_{50}\text{H}_{68}\text{Cl}_2\text{MgN}_4\text{O}_3\text{Ti}_2 \times \text{C}_4\text{H}_8\text{O}$ ,  $M_r = 1038.21 \text{ g mol}^{-1}$ , red prisms, size  $0.40 \times 0.38 \times 0.36 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ ,  $a = 12.232(1)$ ,  $b = 16.573(2)$ ,  $c = 28.708(3) \text{ \AA}$ ,  $\beta = 99.02(1)^\circ$ ,  $V = 5747.7(10) \text{ \AA}^3$ ,  $T = -90^\circ\text{C}$ ,  $Z = 4$ ,  $\rho_{\text{calc.}} = 1.200 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 4.26 \text{ cm}^{-1}$ ,  $F(000) = 2208$ , 12 188 reflections in  $h(-15/0)$ ,  $k(0/20)$ ,  $l(-35/35)$ , measured in the range  $2.29^\circ \leq \theta \leq 26.30^\circ$ , completeness  $\theta_{\text{max}} = 99.8\%$ , 11 630 independent reflections,  $R_{\text{int}} = 0.029$ , 7161 reflections with  $F_o > 4\sigma(F_o)$ , 619 parameters, 0 restraints,  $R1_{\text{obs}} = 0.053$ ,  $wR2_{\text{obs}} = 0.127$ ,

$R1_{\text{all}} = 0.129$ ,  $wR2_{\text{all}} = 0.186$ ,  $\text{GOOF} = 1.095$ , largest difference peak and hole:  $0.652 / -0.922 \text{ e \AA}^{-3}$ .

## 2. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146557 for compound **2**. 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; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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