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Controlled synthesis of $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2TiCl_2$ and $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)TiCl_3$. Crystal structure and reactions of $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)TiCl_3$

Ibrahim Jibril, Sultan Abu-Orabi, Sami A. Klaib
Department of Chemistry, Yarmouk University, Irbid (Jordan)

Wolfgang Imhof and Gottfried Huttner
Anorganisch-Chemisches Institut der Universität Heidelberg, Heidelberg (Germany)

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Abstract

The compounds $(1,3\text{-}^{t}Bu_2C_5H_3)_2TiCl_2$ (I) and $(1,3\text{-}^{t}Bu_2C_5H_3)TiCl_3$ (II) were prepared in good yields from $TiCl_4$ and $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)Li$. Reactions of II with methanol, ethane-1,2-diol, sodium oxalate, and 2-pyrazine carboxylic acid afforded various organotitanium complexes. The crystal structure of II was determined.

Introduction

η^5-Cyclopentadienyltitanium derivatives have played an important role in structural, synthetic and catalytic organometallic chemistry [1–5]. Recently, titanocene dihalides and their derivatives have become of interest in cancer research, the geometries and the nature of the cyclopentadienyl ligand greatly influencing the potency [6,7]. Replacement of one or more of the $C_p(C_5H_5)$ ring hydrogens by alkyl groups has been shown to result in significant changes in reactivity, stability, catalytic activity and other properties owing to changes in both steric and electronic effects at the metal centre [8–13].

Although several alkyl-substituted cyclopentadienyltitanium derivatives have been prepared [8–13] there have been only two reports on $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2)TiCl_2$ [14,15]. As an outcome of our efforts to expand the chemistry of substituted cyclopentadienyltitanium species we describe here a controlled and convenient synthesis of $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)TiCl_2$ and $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)_2TiCl_3$, and present the results of a study of representative reactions of $(1,3\text{-}^{t}Bu_2\text{-}C_5H_3)TiCl_3$ with methanol, ethane-1,2-diol, sodium oxalate, and 2-pyrazine carboxylic acid. These

Correspondence to: Professor I. Jibril, Department of Chemistry, Yarmouk University, Irbid, Jordan.

reactions have given a versatile series of organotitanium complexes containing the $(1,3\text{-}^tBu_2\text{-}C_5H_3)Ti$ moiety.

Experimental

All reactions were conducted under dinitrogen by Schlenk techniques. 1,3-Di-tert-butylcyclopentadiene was prepared as previously described [16,17] and purified by fractional distillation under reduced pressure.

Infrared spectra were recorded on a Pye-Unicam SP3-100 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker WP 80SY spectrometer with TMS as internal standard. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona, USA.

Preparation of $(1,3\text{-}^tBu_2\text{-}C_5H_3)_2TiCl_2$ (I)

To a solution of 17.8 g (0.10 mol) of 1,3-di-tert-butylcyclopentadiene in THF (200 ml) a 1 *M* hexane solution (100 ml) of n-butyllithium was added dropwise at −78°C. The stirred mixture was allowed to warm to room temperature and then 9.5 g (0.05 mol) of anhydrous $TiCl_4$ was added slowly and the mixture was stirred for 0.5 h. The solvent was removed under vacuum at 20°C and the residue washed several times with hexane. The solid remaining was dissolved in chloroform and the solution filtered through Celite then kept overnight at −30°C to give compound I (14.0 g, 59%) as a red powder. Recrystallization from CH_2Cl_2 gave analytically-pure, red needles. M.p. 223–225°C. Found: C, 66.12; H, 8.95; Cl, 15.27. $C_{26}H_{42}Cl_2Tc$ calc.: C, 65.96; H, 8.94; Cl, 14.98%. ^{1}H NMR (δ(ppm), $CDCl_3$): 6.66 (t, 2H); 6.11 (d, 4H); 1.27 (s, 36H).

Preparation of $(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl_3$ (II)

To a (1:3) *p*-xylene/hexane solution of 1,3-di-tert-butylcyclopentadiene (17.8 g, 0.10 mol) a 1 *M* hexane solution (100 ml) of n-butyllithium was added dropwise at −15°C. The stirred mixture was allowed to warm to room temperature (1 h) then cooled to −15°C and anhydrous $TiCl_4$ (19.0 g, 0.10 mol) was slowly added. Stirring was continued for 2 h, then the solvent was removed under vacuum at 20°C. The residue was extracted with 500 ml of hexane and the extract was filtered through Celite, concentrated to 100 ml under vacuum, and kept at −30°C overnight to give orange-red plates of compound II. 23.9 g (70%) yield. M.p. 134–135°C. Found: C, 46.94; H, 6.47; Cl, 32.00. $C_{13}H_{21}Cl_3Ti$ calc.: C, 47.06; H, 6.33; Cl, 32.13%. ^{1}H NMR (δ(ppm), $CDCl_3$): 7.00 (t, 1H), 6.82 (d, 2H); 1.38 (s, 18H).

Preparation of $(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl_2(OCH_3)$ (III)

A benzene solution (100 ml) of $(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl_3$ (1.0 g, 3.0 mmol) was heated to reflux and then treated with anhydrous methanol (0.096 g, 3.0 mmol). Heating was stopped and the mixture was allowed to cool gradually to room temperature. A fine yellow-orange powder separated out, and the solvent was removed by a cannula and the solid washed with hexane and recrystallized from CH_2Cl_2 to give analytically-pure III (0.65 g, 66%). M.p. 94–96°C (dec.). Found: C, 49.50; H, 7.33; Cl, 21.96. $C_{14}H_{24}Cl_2OTi$ calc.: C, 51.38; H, 7.34; Cl, 21.71%. ^{1}H NMR (δ(ppm), $CDCl_3$): 6.57 (m, 3H); 4.48 (s, 3H); 1.34 (s, 18H).

Preparation of [(1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_2$]$_2$-μ-(OCH$_2$CH$_2$O) (IV)

Treatment of (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_3$ (1 g, 3.0 mmol) with ethane-1,2-diol (0.093 g, 1.5 mmol) in a procedure similar to that described for preparation of III gave compound IV as orange-red crystals (0.61 g, 62%). M.p. 93–95°C (dec.). Found: C, 50.98; H, 7.05; Cl, 21.78. $C_{28}H_{46}Cl_4O_2Ti_2$ calc.: C, 51.53; H, 7.06; Cl, 21.78%. ^{1}H NMR (δ(ppm), $CDCl_3$): 6.65 (m, 6H); 3.88 (s, 4H); 1.31 (m, 36H).

Preparation of [(1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_2$]$_2$-μ-(C$_2$O$_4$) (V)

To a THF solution (100 mL) containing 1 g (3.0 mmol) of (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_3$ was added anhydrous sodium oxalate (0.20 g, 1.5 mmol). The mixture was refluxed for 2 h then the solution was filtered through Celite and the solvent evaporated under vacuum at 20°C. The residue was dissolved in CH_2Cl_2 and the solution filtered through Celite and kept at −30°C overnight to yield analytically-pure orange crystals of compound V. 0.44 g (43%) yield. M.p. 184–185°C. Found: C, 49.88; H, 6.21. $C_{28}H_{42}Cl_4O_4Ti_2$ calc.: C, 49.41; H, 6.18%. IR (KBr): 3100w, 2950m, 1680s, 1345s, 1130m. ^{1}H NMR (δ(ppm), $CDCl_3$): 6.90 (t, 2H); 6.65 (d, 4H); 1.39 (s, 36H).

Preparation of (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl (OOC · C$_4$H$_3$N$_2$)$_2$ (VI)

A mixture of (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_3$ (1 g, 3.0 mmol) and 2-pyrazine carboxylic acid (0.37 g, 3.0 mmol) in benzene (100 ml) was stirred overnight at room temperature. The solvent was then evaporated off under vacuum at 20°C and the residue was washed with hexane and dissolved in CH_2Cl_2. The solution was filtered through Celite and kept at −30°C overnight to give purple-red crystals of compound VI. 0.64 g (84%) yield. M.p. 153–155°C (dec.). Found: C, 54.31; H, 5.34; N, 11.01; Cl, 7.25. $C_{23}H_{27}ClN_4O_4Ti$ calc.: C, 54.49; H, 5.33; N, 11.05; Cl, 7.01%. IR (KBr): 3080w, 2980m, 1655s, 1310s, 1140s. ^{1}H NMR (δ(ppm), CD_2Cl_2): 8.41–9.32 (m, 6H); 7.38 (m, 2H); 5.24 (m, 1H); 1.35 (s, 18H).

Crystal structure analysis for (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_3$ (II)

Crystals suitable for the X-ray study were obtained by recrystallization from hexane.

Crystal data: $C_{13}H_{21}Cl_3Ti$; M = 331.2, monoclinic, space group $P2_1/n$ (No. 14) [18] with a 1025.5(2), b 1140.2(3), c 1404.4(3) pm, β 99.40(2)°, V 1620.02 × 10^6 pm^3, d_{calc} 1.36 g cm^{-3}, $Z = 4$, $\mu = 1.0$ mm^{-1}, $F(000)$ 688.

The cell constants and reflections were measured on a Syntex P3 diffractometer with a graphite monochromator, λ(Mo–K_α) 71.073 pm. There were 2414 independent significant reflections ($I > 2\sigma I$). The structure was solved by use of the program SHELXTL-PLUS [19] by direct methods. Hydrogen atoms were placed at calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The refinement converged at $R_1 = 0.0392$, $R_2 = 0.0419$. A list of atomic coordinates is given in Table 1 and one of selected bond distances and bond angles in Table 2. A full list of bond lengths and angles and a list of structure factors are available from the authors.

Discussion

In our attempts to prepare titanium derivatives of 1,3-di-tert-butylcyclopentadiene by reaction of $TiCl_4$ with (1,3-^{t}Bu$_2$-C$_5$H$_3$)Li, we found both (1,3-^{t}Bu$_2$-

Table 1

Atomic coordinates for compound II, with esd's in parentheses

Atom	x	y	z	U_{eq}
Ti(1)	0.08405(7)	0.86625(6)	0.16679(5)	0.0259(2)
Cl(1)	−0.1180(1)	0.9314(1)	0.18087(9)	0.0493(4)
Cl(2)	0.1783(1)	1.03364(9)	0.12875(7)	0.0386(3)
Cl(3)	0.1812(1)	0.83905(9)	0.32040(7)	0.0399(4)
C(1)	0.1049(2)	0.7998(2)	0.0119(2)	0.026(1)
C(2)	−0.0166(2)	0.7568(2)	0.0341(2)	0.027(1)
C(3)	0.0126(2)	0.6779(2)	0.1129(2)	0.023(1)
C(4)	0.1521(2)	0.6721(2)	0.1394(2)	0.021(1)
C(5)	0.2092(2)	0.7475(2)	0.0770(2)	0.023(1)
C(6)	0.3575(4)	0.7551(3)	0.0732(3)	0.029(1)
C(7)	0.3900(5)	0.8560(4)	0.0108(4)	0.058(2)
C(8)	0.3950(4)	0.6398(4)	0.0267(3)	0.048(2)
C(9)	0.4376(4)	0.7655(4)	0.1745(3)	0.046(2)
C(10)	−0.0860(3)	0.5994(3)	0.1545(3)	0.026(1)
C(11)	−0.2287(4)	0.6339(4)	0.1140(3)	0.040(1)
C(12)	−0.0630(4)	0.6056(4)	0.2646(3)	0.039(1)
C(13)	−0.0626(4)	0.4735(3)	0.1221(3)	0.034(1)

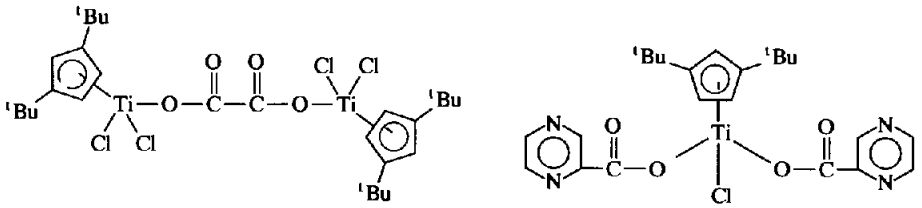
$C_5H_3)_2TiCl_2$ and (1,3-^{t}Bu$_2$-C_5H_3)$TiCl_3$ in substantial amounts. We observed that, in addition to stoichiometric ratio used, the polarity of the reaction medium considerably influences the ratio of these products, increasing polarity of the medium favouring the formation of the bis- over the mono-cyclopentadienyl derivative. In the light of this finding we were able to obtain (1,3-^{t}Bu$_2$-$C_5H_3)_2TiCl_2$ (I) in a better yield (59%) than that (30%) previously obtained by use of THF as solvent [14].

Compound I was characterized from its elemental analysis and ^{1}H NMR spectrum which was fully consistent with that previously reported [14]. Moreover (1,3-^{t}Bu$_2$-C_5H_3)$TiCl_3$ (II) was prepared, for the first time, in good yield (70%) by using a non-polar reaction medium (*p*-xylene/hexane). Compound II is relatively stable in the solid state but unstable in solution in presence of air or moisture. It was characterized by elemental analysis, ^{1}H NMR spectroscopy, and X-ray diffraction.

Table 2

Selected bond distances (Å) and bond angles (°) for compound II

Ti(1)–Cl(1)	2.240(1)	Cl(1)–Ti(1)–Cl(2)	100.4(1)
Ti(1)–Cl(2)	2.243(1)	Cl(1)–Ti(1)–Cl(3)	103.5(1)
Ti(3)–Cl(3)	2.245(1)	Cl(2)–Ti(1)–Cl(3)	101.9(1)
Ti(1)–C(1)	2.345(2)		
Ti(1)–C(2)	2.338(2)		
Ti(1)–C(3)	2.354(2)		
Ti(1)–C(4)	2.371(2)		
Ti(1)–C(5)	2.366(3)		



V VI

Fig. 1. Proposed structures for $[(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl_2]\text{-}\mu\text{-}(C_2O_4)$ (V) and $(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl(OOC\text{-}C_4H_3N_2)_2$.

Compound II could be one of the most useful precursors for the synthesis of a large variety of organometallic titanium complexes containing a cyclopentadienyl ligand bearing bulky substituents, of interest since the presence of two tert-butyl groups on the Cp-ring can be expected to influence the properties of the complexes. Thus some representative reactions of compound II with methanol, ethane-1,2-diol, sodium oxalate, and 2-pyrazine carboxylic acid were examined. Each of these reagents is representative of a class of compounds that might be the subject of a detailed study in the future.

The reactions of compound II with methanol and ethane-1,2-diol, used in 1:1 and 2:1 (M:L) molar ratio, respectively, produced the orange complexes $(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl_2(OCH_3)$ (III) and $[(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl_2]_2\text{-}\mu\text{-}(C_2H_4O_2)$ (IV) in good yields.

Compounds III and IV were characterized from their elemental analyses and ^1H NMR spectra.

Treatment of compound II with sodium oxalate and 2-pyrazine carboxylic acid afforded the compounds $[(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl_2]_2\text{-}\mu\text{-}(C_2O_4)$ (V) and $(1,3\text{-}^tBu_2\text{-}C_5H_3)TiCl(OOC\text{-}C_4H_3N_2)_2$ (VI), respectively. The elemental analyses and ^1H NMR spectra were consistent with formulae shown. The assignment of the structures shown (Fig. 1) was based on their infrared spectra.

A commonly used criterion [20–23] for distinguishing the M–OOCR coordination mode is the frequency difference between the asymmetric and symmetric OCO stretching modes ($\Delta\nu = \nu(OCO)_{as} - \nu(OCO)_s$), which is > 200 cm^{-1} for monodentate bonding and < 105 cm^{-1} for chelate bonding. Since the difference between the asymmetric and symmetric stretching frequencies in compounds V ($1680 - 1345 = 335$) and VI ($1665 - 1310 = 355$) is > 200 cm^{-1}, the monodentate mode of bonding is most likely. Moreover, lower values for the asymmetric OCO stretching frequency for the monodentate carboxylate complexes can be observed, as in our case, and this is attributed to weak interactions of the carboxyl (C=O) group with the metal centre [22].

Finally, it is noteworthy that under the conditions used the reaction of compound II with 2-pyrazine carboxylic acid gave only compound VI even though a 1:1 molar ratio was used. This feature is still under investigation; a preliminary study of the corresponding reaction with 2-pyridine carboxylic acid has revealed similar behaviour in that case.

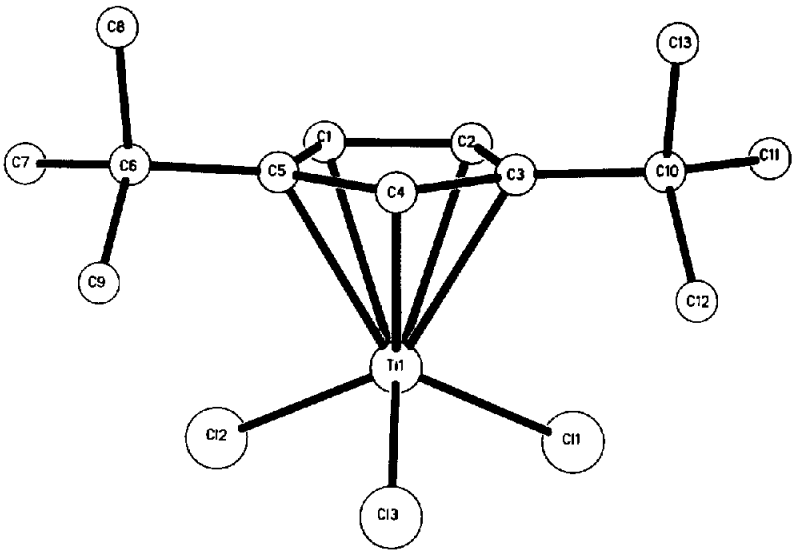


Fig. 2. Molecular structure of (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_3$.

Molecular structure of (1,3-^{t}Bu$_2$-C$_5$H$_3$)TiCl$_3$ (II)

The molecular structure of compound II is shown in Fig. 2. Selected bond distances and bond angles are given in Table 2 [24*].

The molecule has a piano-stool configuration similar to that revealed by the X-ray structure of the unsubstituted analogue [25]. The cyclopentadienyl ring is practically planar, with average Ti–C bond distances of 2.35 Å. The quaternary carbon atoms of the tert-butyl groups are nearly co-planar with the cyclopentadienyl ring. Two main differences from the unsubstituted analogue are observed: shorter Ti–Cl bonds (average TiCl: 2.24; 2.29 Å) bonds and smaller Cl–Ti–Cl bond angles (average: 101.9; 103°). Both differences can be attributed to the steric and to the electronic effects of the tert-butyl groups. The smaller Cl–Ti–Cl bond angles may be the result of the steric requirements of the bulky tert-butyl groups, while the shorter Ti–Cl bonds may be the result of the electronic effects of the electron releasing tert-butyl groups, which increase the basicity of the Cp-ring, so leading to a relatively ionic Ti–Cp bond. This in turn results in a stronger Ti–Cl bond due to the stronger interaction between the titanium Lewis centre and the σ and π donor Cl atoms [14].

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* Reference number with asterisk indicates a note in the list of references.

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