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The synthesis of (η^5-cyclopentadienyl)titanium(IV) alkoxides by alcoholysis of the Ti–π-ligand bond in permethyl η^3:η^4-allyldiene-(η^5-cyclopentadienyl)titanium(II)

Karel Mach [a], Jiří Kubišta [a], Libor Trojan [b], Ivana Císařová [b], Petr Štěpnička [b,*]

[a] *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic*

[b] *Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic*

Abstract

The η^3:η^4-allyldiene-(η^5-cyclopentadienyl)titanium(II) complex [Ti(η^5-C_5Me_5){η^3:η^4-$C_5Me_3(CH_2)_2$}] (**1**) reacts with three molar equivalents of substituted propargylic alcohols FcC≡CCMe$_2$(OH) (**2a**) and PhC≡CCH$_2$OH (**2b**) at elevated temperature to give (η^5-pentamethylcyclopentadienyl)titanium(IV) alkoxides [Ti(η^5-C_5Me_5)(FcC≡CCMe$_2$O-κO)$_3$] (**3a**) and [Ti(η^5-C_5Me_5)(PhC≡CCH$_2$O-κO)$_3$] (**3b**), respectively. The crystal structure of **3a** has been determined by single-crystal X-ray diffraction.

Keywords: Titanium; Cyclopentadienyl; Ferrocene; Alkyne; Alkoxide; X-ray crystallography

1. Introduction

Electron-poor cyclopentadienyltitanium compounds willingly react with polar molecules. Except for a simple coordination of a Lewis donor onto the titanium atom that produces a more stable adduct, the primary reactions are frequently followed by molecular rearrangements, oxidative addition, insertion and C–H activation processes, Ti–π-ring bond cleavage and also by consecutive addition reactions [1]. Recently [2], we have reported about the insertion of alkynylketones RC≡CC(O)Me, where R = Fc (ferrocenyl) and SiMe$_3$, into Ti–C bond in η^5-pentamethylcyclopentadienyl-(η^3:η^4-trimethylallyldiene)titanium(II) (**1**) [3]. In this contribution, we describe alcoholysis of **1** with substituted propargylalcohols FcC≡CCMe$_2$(OH) (**2a**) and PhC≡CCH$_2$OH (**2b**), which affords (η^5-pentamethylcyclopentadienyl)titanium(IV) alkynylalkoxides [Ti(η^5-C_5Me_5)(FcC≡CCMe$_2$O-κO)$_3$] (**3a**) and [Ti(η^5-C_5Me_5) (PhC≡CCH$_2$O-κO)$_3$] (**3b**), respectively, and the crystal structure of **3b**.

2. Results and discussion

The reaction of **1** with alcohol **2a** proceeds reasonably well only at elevated temperatures. As revealed by NMR analysis of crude reaction mixtures obtained at various **1**:**2a** molar ratios, the educts react in 1:3 molar ratio to give **3a** (Scheme 1), while a possible excess of either educt remains unreacted. Thus, the reaction can be formulated as:

$$\mathbf{1} + 3\ \mathbf{2a} \rightarrow [\mathrm{Ti}(\eta^5\text{-}C_5Me_5)(\mathrm{FcC{\equiv}CCMe_2O}\text{-}\kappa O)_3]\ (\mathbf{3a}) + C_5Me_5H$$

and rationalized as a protonolysis of both Ti–CH$_2$ bonds in **1** with two molecules of **2a** followed by a cleavage of the Ti–η^5-C_5Me_5 bond with the third alcohol equivalent to afford **3a**. A reaction of **1** with three equivalents of **2a** furnished alkoxide **3a** in 65% isolated as a dark yellow orange crystalline solid, which was characterized by spectral methods and X-ray crystallography.

Alcohol **2b** reacts analogously and under similar conditions to give alkoxide [Ti(η^5-C_5Me_5)(PhC≡CCH$_2$O-κO)$_3$] (**3b**), which was obtained as a light yellow oil and identified by spectral methods. A similar reaction between **1** and excess MeOH also proceeds with the cleavage of the Ti–η^5-C_5Me_5 bond, but yields a mixture

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[*] Corresponding author. Tel.: +420-221-951-260; fax: +420-221-951-253.

E-mail address: stepnic@natur.cuni.cz (P. Štěpnička).

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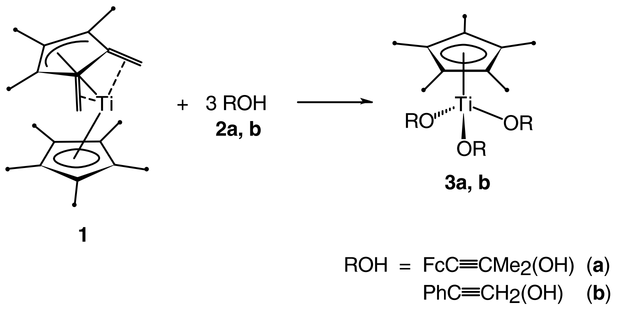

Scheme 1.

containing several diamagnetic Ti(η^5-C_5Me_5) methoxides including [Ti(η^5-C_5Me_5)$(OMe)_3$], which was identified by NMR spectra of the mixture [4], and the least hexane-soluble, paramagnetic complex [{(η^5-C_5Me_5)Ti$(OMe)_2$(μ-OMe)}$_2$], which was isolated as a brown crystalline solid and characterized by X-ray diffraction [5].

The alcoholysis of **1** represents an alternative synthetic approach to the preparation (η^5-cyclopentadienyl)titanium tris(alkoxides) as they were so far synthesized usually by salt metathesis of chlorides [$TiCl_3$(η^5-$C_5R^1_5$)] and [TiCl$(OR^2)_3$] with alkali metal alkoxides and cyclopentadienides, respectively [6]. Alkoxides [Ti(η^5-$C_5R^1_5$)$Cl_{3-x}(OR^2)_x$] ($x = 1 - 3$) are of practical importance, in combination with excess methylalumoxane (MAO), because they provide efficient catalysts for syndiospecific polymerization of styrene [7].

2.1. The crystal structure of **3b**

As revealed by X-ray crystallography, complex **3a** possesses the expected three-legged piano stool structure (Fig. 1, Table 1). The Ti–Cg distance is 2.075(1) Å and the titanium atom is displaced by 0.746(1) Å from the plane of the three ligating oxygen atoms. The cyclopentadienyl and {O1O2O3} planes are slightly tilted from a coplanar arrangement at a dihedral angle of 9.4(1)°. This is also reflected by a variance among the O–Ti–O and Cg–Ti–O angles.

The Ti–O distances slightly differ for the three alkoxide units, but compare well to those in analogous phenoxides [Ti(η^5-C_5H_5)(OC_6H_3-2,6-$i$$Pr_2$)$_3$] (1.79(2), 1.80(2), 1.80(2) Å [8]) and [Ti(η^5-C_5Me_5)(OC_6H-2,3,5,6-F_4)$_3$] (1.826(3), 1.830(3) and 1.867(3) Å [9]). This variation of the Ti–O bond lengths as well as differences in the geometries of the alkoxide moieties (see Table 1) can most likely be attributed to a steric crowding between the bulky cyclopentadienyl and the alkoxide ligands. The three ferrocenyl units adopt different orientations towards the Ti(η^5-C_5Me_5) unit (see dihedral angles ϕ in Table 1 and the dihedral angles between the substituted ferrocene cyclopentadienyls: 84.5(1)°, 81.0(1)°, and 36.0(1)° for the pairs of alkoxide moieties 1–2, 1–3, and 2–3, respectively).

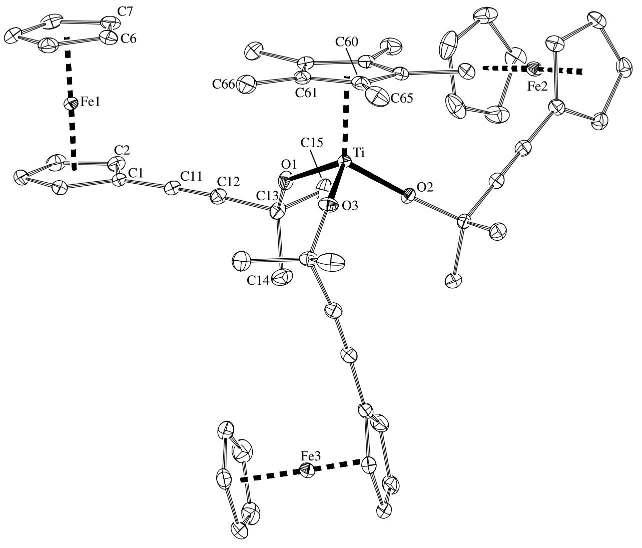

Fig. 1. A view of the molecular structure of alkoxide **3a** drawn at 30% probability level. For clarity, labels of only pivotal and its adjacent carbon atoms in cyclopentadienyl rings are given. Full atom numbering is shown only for alkoxide unit 1 because the labelling scheme adopted for alkoxide units 2 and 3 is analogous, the atom labels in these moieties being obtained by adding 20 and 40 to the respective atom number, respectively. All hydrogen atoms were omitted.

Table 1
The selected geometric parameters for **3a** (Å) and (°)[a,b]

Alkoxide unit	1	2	3
Ti–O	1.830(2)	1.791(1)	1.830(2)
Cg–Ti–O	113.19(5)	119.06(5)	110.56(6)
ϕ	4.4(1)	82.9(1)	77.3(1)
Fe–Cg (subst.)	1.652(1)	1.651(1)	1.647(1)
Fe–Cg (unsubst.)	1.652(1)	1.656(1)	1.655(1)
Cg–Fe–Cg	178.84(6)	177.81(6)	178.58(6)
O–C	1.417(3)	1.423(2)	1.411(2)
O–**C**–**C**	1.485(3)	1.483(3)	1.488(3)
C≡C	1.192(3)	1.193(3)	1.197(3)
C≡**C**–**C**(Fc)	1.431(3)	1.435(3)	1.436(3)
O–C–C	109.6(2)	108.6(2)	111.6(2)
C–C≡C	173.3(2)	179.4(2)	173.7(2)
C≡C–C(Fc)	175.9(2)	176.2(2)	176.4(2)

[a] Cp and Cg denote a cyclopentadienyl ring and its centroid, respectively. ϕ is the dihedral angle subtended by the Cp(Ti) and the respective substituted Cp(Fe) cyclopentadienyl least-squares planes.

[b] Further data: Ti–Cg 2.075(1) Å; O(1)–Ti–O(2) 102.50(6)°, O(1)–Ti–O(3) 105.34(7)°, O(2)–Ti–O(3) 104.96(7)°.

3. Experimental

3.1. General comments

The synthesis of alcohols **2** was carried out under argon; their subsequent reactions with **1** were performed on a high vacuum line using sealed all-glass devices equipped with breakable seals. Diethyl ether and acetone were dried over sodium metal and potassium carbonate, respectively, and distilled under argon. Toluene and hexane were dried by refluxing with $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4C_5H_4)\{Ti(\mu\text{-}H)(\eta^5\text{-}C_5H_5)\}_2]$ [10] on the vacuum line. Complex **1** was prepared by thermolysis of $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ [11].

Samples for EI MS measurements, X-ray diffraction analysis and melting point determinations were inserted into glass capillaries (Lindenmann glass capillaries for X-ray analyses) under purified nitrogen in a Labmaster 130 glovebox (mBraun) and sealed. KBr pellets were prepared and placed into an air-protecting cuvette in the glovebox. ^1H (399.95 MHz) and ^{13}C (100.58 MHz) NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer in C_6D_6 solutions at 25 °C. Chemical shifts (δ/ppm) are given relative to the solvent signal (δ_H 7.15, δ_C 128.0). EI MS spectra were recorded at 70 eV on a VG-7070E mass spectrometer.

3.2. Synthesis of $FcC{\equiv}CCMe_2(OH)$ (**2a**)

A solution of ethynylferrocene (2.20 g, 10.5 mmol) in dry diethyl ether (40 ml) was cooled to −30 °C (temperature in bath) and treated with LiBu (4.6 ml 2.5 M in hexanes, 11.5 mmol). After stirring for 30 min at −30 °C, acetone (1.0 ml, 13.5 mmol) was slowly added to the formed acetylide solution and stirring was continued for another 2.5 h at room temperature. The reaction was terminated by addition of 5% aqueous H_3PO_4 (10 ml), the organic phase was separated, washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The dark orange residue was purified by chromatography on a short silica gel column using first toluene to remove a small amount of unreacted ethynylferrocene (a yellow band) and then diethyl ether to elute the product (red band). Evaporation of the second fraction afforded **2a** as rusty orange solid. Yield: 2.45 g, 88%.

NMR (C_6D_6): δ_H 1.47 (s, 6 H, $C\mathit{Me}_2$), 1.66 (s, 1 H, $O\mathit{H}$), 3.88 (apparent t, 2 H, $C_5\mathit{H}_4$), 4.06 (s, 5 H, $C_5\mathit{H}_5$), 4.37 (apparent t, 2 H, $C_5\mathit{H}_4$); δ_C 31.9 ($C\mathit{Me}_2$), 65.4, 65.7 ($\mathit{C}{\equiv}\mathit{C}CMe_2O$ and C_{ipso} C_5H_4); 68.9 ($\mathit{C}H$ C_5H_4), 70.2 (C_5H_5), 71.7 ($\mathit{C}H$ C_5H_4), 80.6, 91.4 ($\mathit{C}{\equiv}\mathit{C}CMe_2O$ and C_{ipso} C_5H_4). IR (KBr): $\tilde{\nu}$/cm^{-1} 3309 br s, 3093 w, 2975 s, 2930 w, 2232 br w, 1453 w, 1386 m, 1362 m, 1273 m, 1196 s, 1165 s, 1138 vs, 1107 m, 1040 w, 1021 m, 1001 m, 967 m, 934 s, 821 vs, 650 br w, 511 m, 493 m, 482 s, 459 w. Anal. calcd. for $C_{15}H_{16}FeO$: C, 67.19%; H, 6.01%. Found: C, 67.22%; H, 5.81%.

3.3. Synthesis of $PhC{\equiv}CCH_2OH$ (**2b**)

Butyl lithium (22 ml 2.5 M in hexanes, 55 mmol) was slowly added to an ice-cooled solution of phenylethyne (5.11 g, 50 mmol) in dry diethyl ether (50 ml). After the resulting suspension of lithium acetylide was stirred for 5 min at 0 °C, paraformaldehyde (3.0 g, 0.10 mol) was added and stirring was continued overnight at room temperature. Then, the reaction mixture was quenched by saturated aqueous NH_4Cl and stirring for 1 h. The organic phase was separated, washed with saturated aqueous NH_4Cl, dried over $MgSO_4$ and evaporated to give a viscous oily residue which was distilled under vacuum (89–91 °C at 0.7 Torr) to afford **2b** as a colourless viscous liquid (5.18 g, 78%). Prior to the reaction with **1**, alcohol **2b** was degassed and distributed into ampoules with breakable seals by distillation under vacuum.

NMR ($CDCl_3$): δ_H 3.47 (br s, 1 H, $O\mathit{H}$), 4.30 (s, 2 H, $C\mathit{H}_2$), 6.93–7.45 (m, 5 H, Ph); δ_C 51.2 ($\mathit{C}H_2$), 85.6, 88.5 ($\mathit{C}{\equiv}\mathit{C}$), 123.4 ($\mathit{C}_{ipso}$ Ph), 128.4, 128.5, 131.9 ($\mathit{C}H$ Ph). GC-MS, m/z (relative abundance): 132 (98, $M^{+\cdot}$), 131 (100), 115 (46, $[M\text{–}OH]^+$), 103 (33, $[M\text{–}CHO]^+$), 77 (62, $C_6H_5^+$), 51 (23). IR (neat): $\tilde{\nu}$/cm^{-1} ν_{OH} 3335 br s; ν_{CH} 3082 w, 3060 w, 2918 w, 2865 w; $\nu_{C\equiv C}$ 2238 br w; 1598 m, 1490 s, 1442 m, 1359 br m, 1257 m, 1032 composite s, 953 s, 756 s, 691 s.

3.4. Synthesis of $[Ti(\eta^5\text{-}C_5Me_5)\ (FcC{\equiv}CCMe_2O\text{-}\kappa O)_3]$ (**3a**)

A solution of **1** in toluene (0.22 g, 0.7 mmol in 5.0 ml) was added to a solution of **2a** (0.536 g, 2.0 mmol) in the same solvent (20 ml) and the mixture was heated to 120 °C for 8 h. All volatiles were removed under vacuum (at max. 80 °C) and the residue was extracted with hexane. A small amount of blue **1** was extracted at room temperature, while a repeated extraction with hot hexane and a subsequent evaporation yielded a residue which was recrystallized from toluene to afford **3a** as a dark yellow orange crystalline solid. Yield: 0.45 g (65%).

M.p. 139 °C. NMR (C_6D_6): δ_H 1.82 (s, 18 H, $C\mathit{Me}_2$), 2.36 (s, 15 H, $C_5\mathit{Me}_5$), 3.92 (apparent t, 6 H, $C_5\mathit{H}_4$), 4.14 (s, 15 H, $C_5\mathit{H}_5$), 4.43 (apparent t, 6 H, $C_5\mathit{H}_4$); δ_C 12.7 ($C_5\mathit{Me}_5$), 34.5 ($C\mathit{Me}_2$), 66.8 ($\mathit{C}{\equiv}\mathit{C}CMe_2O$ and C_{ipso} C_5H_4), 68.7 ($\mathit{C}H$ C_5H_4), 70.2 (C_5H_5), 71.5 ($\mathit{C}H$ C_5H_4), 75.9, 79.6, 93.8 ($\mathit{C}{\equiv}\mathit{C}CMe_2O$ and C_{ipso} C_5H_4), 123.4 (C_5Me_5). EI-MS (250 °C): m/z (relative abundance) 984 ($M^{+\cdot}$; 0.2), 830 (7), 829 (10), 828 (6), 695 (8), 556 (7), 502 (9), 461 (10), 460 (25), 423 (17), 422 (65), 421 (42), 420 (75), 418 (11), 319 (10), 318 (28), 317 (50), 316 (54), 315 (12), 300 (12), 268 (12), 253 (12), 252 (44), 251 ($[FcC{\equiv}CCMe_2]^+$; 90), 250 (46), 242 (13), 240 (16), 237 (12), 236 (19), 212 (14), 211 (15), 210 ($[FcC{\equiv}CH]^{+\cdot}$; 42), 186 ($[FcH]^{+\cdot}$; 36), 179 (12), 178 (14), 152 (18), 136 (17), 135 ($[C_5Me_5]^+$; 45), 133 (15), 129 (14), 128 (13), 121 ($[C_5H_5Fe]^+$; 100), 120 (13), 119 (43), 115 (14), 107 (10), 105 (24), 95 (14), 93 (12), 91 (23), 89 (11), 83 (13), 81 (13), 79 (17), 77 (28), 71 (13), 69 (20), 67 (14), 65 (13), 58 (22), 57 (29), 56 (Fe^+; 51), 55 (42). IR (KBr): $\tilde{\nu}$/cm^{-1} 3096 w, 3088 w, 2975 s, 2922 m, 2854 w, 2233 w, 2208 vw, 1453 br m, 1374 m, 1352 m, 1270 m, 1194 s, 1166 vs, 1137 vs, 1027 vs, 1002 vs, 946 s, 898 m, 821 s, 781 m, 616 m, 520 m, 484 s, 470 m, 450 m, 430 m, 420 m.

3.5. Synthesis of $[Ti(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CCH_2O\text{-}\kappa O)_3]$ (**3b**)

A solution of **1** in toluene (0.31 g, 1.0 mmol in 7.5 ml) was mixed with **2b** (0.5 ml, 3.4 mmol). The mixture was heated in a sealed ampoule to 100 °C for 10 h whereupon the originally blue solution turned green and, finally, clear yellow. All volatiles were distilled off under vacuum (finally at 100 °C) and the resulting yellow oil was distributed for the measurement of EI-MS, NMR and IR spectra. All attempts to crystallize the compound from a saturated hexane solution at low temperature failed. The yield was not determined.

NMR (C_6D_6): δ_H 2.09 (s, 15 H, C_5Me_5), 5.21 (s, 6 H, CH_2), 6.91–7.54 (m, 15 H, *Ph*); δ_C 11.4 (C_5Me_5), 61.8 (CH_2), 84.7, 90.5 ($C{\equiv}C$); 124.3 (C_5Me_5), 124.0 (C_{ipso} Ph), 128.1, 128.5, 131.9 (*C*H Ph). EI-MS (120 °C): *m/z* (relative abundance) 576 ($M^{+\cdot}$, 2), 444 ($[M-PhC{\equiv}CCH_2OH]^+$; 2.5), 414 (4), 405 (5), 404 (15), 403 (6), 246 (6), 245 (5), 218 (6), 217 (10), 215 (8), 202 (6), 136 (17), 135 (11), 121 (24), 119 (15), 116 (17), 115 ($[PhC{\equiv}CCH_2]^+$; 100), 105 (23), 104 (6), 103 (12), 102 (17), 91 (17), 89 (6), 77 (9), 40 (39). IR (neat): $\tilde{\nu}/cm^{-1}$ 3080 (w), 3055 (m), 3033 (w), 3020 (w), 2956 (m), 2909 (s), 2837 (s), 2238 (w), 1598 (m), 1489 (vs), 1442 (s), 1376 (w), 1351 (vs), 1256 (m), 1113 (vs,b), 1070 (vs,b), 1028 (s,sh), 999 (m), 958 (m), 914 (w), 755 (vs), 724 (w), 691 (vs), 661 (s), 619 (m), 532 (s), 494 (m).

3.6. X-ray crystallography

Structure determination for **3a**: $C_{55}H_{60}Fe_3O_3Ti$ ($M = 984.5$); triclinic, space group $P-1$ (no. 2); $T = 150$ K, $a = 9.7886(2)$, $b = 15.1418(3)$, $c = 17.2486(2)$ Å; $\alpha = 73.735(1)°$, $\beta = 89.423(1)°$, $\gamma = 73.409(1)$ °; $V = 2345.23(7)$ Å^3, $Z = 2$, $D_c = 1.39$ g cm^{-3}; orange-brown plate from toluene, $0.25 \times 0.25 \times 0.75$ mm^3 (measured in Lindenmann glass capillary under nitrogen), $2\theta_{max} = 55°$, data completeness 98.1%; 44 775 collected, 10 575 unique and 9221 observed $[I_0 > 2\sigma(I_0)]$ diffractions (Nonius KappaCCD diffractometer, Mo-Kα radiation, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 1.117 mm^{-1}).

The structure was solved by direct methods (SIR92, [12]) and refined by weighted full-matrix least-squares on F^2 (SHELXL97, [13]). All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included into calculated positions (riding model). 559 parameters, final $R = 3.48\%$, $wR = 7.93\%$ for observed diffractions, $R = 4.33\%$ for all data, $R_{int} = 3.7\%$; residual electron density +0.73, −0.59 e Å^{-3}.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-206346). The data can be obtained upon request to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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[4] NMR (C_6D_6): δ_H 1.97 (s, 15 H, C_5Me_5), 4.10 (s, 9 H, O*Me*); δ_C 10.8 (C_5Me_5), 61.4 (O*Me*), 121.6 (C_5Me_5). Considering the signal intensities and similarity with the above chemical shifts, the other component in the mixture was tentatively assigned the μ-oxo structure, $[(\mu\text{-}O)\{Ti(\eta^5\text{-}C_5Me_5)(OMe)_2\}_2]$. This compound may originate from a reaction with traces of water present in methanol; NMR (C_6D_6): δ_H 2.05 (s, 15 H, C_5Me_5), 4.13 (s, 6 H, O*Me*); δ_C 11.0 (C_5Me_5), 61.5 (O*Me*), 121.8 (C_5Me_5).

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