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Note

Synthesis and structure of titanium alkoxides based on tetraphenyl substituted 2,6-dimethanolpyridine moiety

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Abstract

Novel titanocanes and spirobititanocanes based on 2,6-bis[hydroxy(diphenyl)methyl]pyridine (**1a**) and 2,6-di(hydroxymethyl)pyridine (**1b**) – $[2,6\text{-}C_5H_3N(CPh_2O)_2]Ti(O\text{-}i\text{-}Pr)_2$ (**2a**), $[2,6\text{-}C_5H_3N(CPh_2O)_2]_2Ti$ (**3a**), $[2,6\text{-}C_5H_3N(CH_2O)_2]_2Ti$ (**3b**), $[2,6\text{-}C_5H_3N(CPh_2O)_2]TiCl_2$ (**4**) – as well as the closely related *N*-phenyl derivative $PhN(CH_2CH_2O)_2Ti(Cl)Cp$ (**5**) have been synthesized. Complexes **2**–**5** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis data. The molecular structure of **3a** was determined by X-ray structure analysis.

Keywords: 2,6-Pyridinedimethanol ligand; Transannular interaction; Alkoxides; Crystal structure

1. Introduction

During the last five decades, alkoxytitanium derivatives have found widespread application as catalysts in various organic processes [1–8]. Usually, in fine organic reactions, tetraalkoxytitanium derivatives are used jointly with co-catalysts, such as (R)-BINOL or (L)-(+)-tartrate which form during the reaction the catalytic active species due to the substitution of alkoxy groups at titanium center [9–13]. However, the structure of these species is postulated and studied in detail very seldom. At the same time the investigations of such species are important because they give new information about the structural titanium chemistry as well as about an organic reaction mechanism. It should be noted that there are several ligand types which form enough stable complexes with $Ti(O\text{-}i\text{-}Pr)_4$ to study their structure and reactivity. A very promising class of titanium alkoxides which is suitable for relationship "structure – catalytic property" is compounds containing an additional intramolecular donor group. This group may form the transannular bond with titanium center. The presence of such a bond in molecules allows to govern the structural and electronic parameters of the titanium derivative such as coordination number of Ti atom as well as the type of its coordination polyhedron and Lewis acidity and hence to vary the catalytic properties of titanium compound. Among these compounds the derivatives of trialkanolamines as ligands (titanatranes) have been investigated in considerable extent. The different structural features and catalytic applications were found for these substances (see key references and references cited therein) [14–18]. The derivatives of dialkanolamines (titanocanes) and monoalkanolamines are less studied [19–30]. However, these classes of compounds could be more promising objects for investigations due to their greater chemical and structural flexibility. Titanocanes derivatives containing pyridine moiety (for example 2,6-di(hydroxymethyl)pyridine) are particularly interesting due to the special electronic and steric properties of the pyridine group. Although these derivatives were previously

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prepared [31], their structural investigations are not known to date.

In continuation of our studies on titanatrane and titanocane chemistry [32,33], we present here the synthesis and characterization of new cyclic titanium alkoxides with transannular interaction. Their structure in solution is discussed based on NMR spectroscopy data. The structure of compound **3a** was determined by single-crystal X-ray analysis.

2. Experimental

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled before use. Ti(O-*i*-Pr)$_4$ (Aldrich) was distilled before use. 2,6-Di(hydroxymethyl)pyridine (**1b**) (Aldrich) was used as supplied. 2,6-Bis[hydroxy(diphenyl)methyl]pyridine (**1a**) [34], $TiCl_2(NMe_2)_2$ [35] and $CpTiCl_3$ [36] were synthesized according to the literature procedures. $CDCl_3$ was obtained from Deutero GmbH and dried over P_4O_{10}. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 spectrometer (in $CDCl_3$ at 295 K unless otherwise stated). Chemical shifts in the ^{1}H and ^{13}C NMR spectra are given in ppm relative to internal Me_4Si. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University.

2.1. Reaction of Ti(O-i-Pr)$_4$ with 2,6-bis[hydroxy(diphenyl)methyl]pyridine (*1a*); the formation of [2,6-Py(CPh$_2$O)$_2$]Ti(O-i-Pr)$_2$ (*2a*)

To a solution of **1a** (1.0 g, 2.08 mmol) in chloroform (25 mL) at 20 °C was added dropwise Ti(O-*i*-Pr)$_4$ (0.62 mL, 2.08 mmol), and the resulting mixture was stirred and refluxed for 5 h. The solvent was then evaporated under reduced pressure to leave a white powder. The powder was recrystallized from a mixture of methylene chloride (3 mL) and hexane (0.5 mL). Compound **2a** was isolated in 85% yield (contains a small amount of **3a**; ^{1}H and ^{13}C NMR spectroscopy data). ^{1}H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 7.78 (t, $^3J_{HH} = 7.8$ Hz, 1H, H1), 7.34 (d, $^3J_{HH} = 7.8$ Hz, 2H, H2, H2′), 7.39 (m, 8H), 7.26 (m, 12H), 4.47 (sept, $^3J_{HH} = 6.1$ Hz, 2H, OCH), 0.99 (d, $^3J_{HH} = 6.1$ Hz, 12H). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ (ppm): 171.29 (C3, C3′), 146.70 (C-*i*), 140.23 (C1), 127.90 (C-*m*), 127.50 (C-*o*), 127.22 (C-*p*), 121.46 (C2, C2′), 95.92 (C4, C4′), 76.19 (C5, C5′), 25.82 (C6, C6′). The satisfactory results of elemental analyses were not obtained due to the presence of traces of **3a**.

2.2. Synthesis of [2,6-Py(CPh$_2$O)$_2$]$_2$Ti (*3a*)

2.2.1. Method A

Ti(O-*i*-Pr)$_4$ (0.14 mL, 0.45 mmol) was added dropwise to a solution of **1a** (400 mg, 0.90 mmol) in toluene (10 mL). After 15 h refluxing, the solvent was evaporated resulting in 0.40 g (95%) of a white solid. Suitable crystals were obtained by slow evaporation of solution of **3a** in toluene. *Anal.* Calc. for $C_{62}H_{46}N_2O_4Ti$: C, 79.99; H, 4.98; N, 3.01. Found: C, 79.40; H, 5.22; N, 2.93%. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 7.68 (t, $^3J_{HH} = 7.8$ Hz, 2H, H1), 7.32 (d, $^3J_{HH} = 7.8$ Hz, 4H, H2, H2′), 7.22 (m, 16H), 7.10 (m, 8H), 7.01 (m, 16H). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ (ppm): 172.17 (C3, C3′), 147.43 (C-*i*), 140.04 (C1), 128.13 (C-*m*), 127.66 (C-*o*), 126.62 (C-*p*), 121.14 (C2, C2′), 98.48 (C4, C4′).

2.2.2. Method B

To a solution of **1a** (0.8 g, 1.80 mmol) in toluene (25 mL) at −78 °C was added dropwise a solution of BuLi in hexane (1.90 mmol), and the resulting mixture was stirred at the same temperature for 1 h. Then the temperature was raised to 0 °C and maintained for 2 h. $TiCl_4$ (0.19 mL, 1.80 mmol) was added dropwise at −78 °C to the obtained suspension, and the mixture was stirred overnight. The solution was filtered and the solvent was evaporated under reduced pressure to leave a white powder. The powder was recrystallized from toluene yielding 0.46 g (54%) of compound **3a**.

2.3. Synthesis of [2,6-Py(CH$_2$O)$_2$]$_2$Ti (*3b*)

Ti(O-*i*-Pr)$_4$ (1.22 g, 4.3 mmol) was added dropwise to a solution of **1b** (0.60 g, 4.3 mmol) in DMSO (20 mL). After 45 h of stirring, the formed solid was filtered and washed with dichloromethane resulting in 0.62 g (90%) of an orange solid. *Anal.* Calc. for $C_{14}H_{14}N_2O_4Ti$: C, 52.20; H, 4.38; N, 8.70. Found: C, 52.05; H, 4.48; N, 8.59%. ^{1}H NMR (400.1 MHz, DMSO-d_6) δ (ppm): 8.05 (t, $^3J_{HH} = 7.6$ Hz, 2H, H1), 7.50 (d, $^3J_{HH} = 7.6$ Hz, 4H, H2, H2′), 5.53 (s, 8H, CH_2). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ (ppm): 167.91 (C3, C3′), 141.04 (C1), 116.90 (C2, C2′), 77.38 (C4, C4′).

2.4. Synthesis of [2,6-Py(CPh$_2$O)$_2$]TiCl$_2$ (*4*)

A solution of **1a** (1.07 g, 2.42 mmol) in chloroform (20 mL) was added to a suspension of $TiCl_2(NMe_2)_2$ (0.5 g, 2.42 mmol) in chloroform (40 mL) at 20 °C. The mixture was stirred for 60 h. After that, the mixture was filtered through Celite and the solvent was evaporated in vacuum. The crude product was recrystallized from methylene chloride obtaining 0.27 g (20%) of a fine white solid. *Anal.* Calc. for $C_{31}H_{23}Cl_2NO_2Ti$: C, 66.45; H, 4.14; N, 2.50. Found: C, 65.24; H, 3.76; N, 2.03%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.99 (t, $^3J_{HH} = 7.8$ Hz, 2H, H1), 7.53 (d, $^3J_{HH} = 7.8$ Hz, 4H, H2, H2′), 7.40 (m, 8H), 7.27 (m, 12H). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ (ppm): 170.85 (C3, C3′), 143.57 (C-*i*), 142.20 (C1), 128.21 (C-*m*), 128.00 (C-*o*), 127.72 (C-*p*), 122.08 (C2, C2′), 98.71 (C4, C4′).

2.5. Attempt at synthesis of [2,6-Py(CPh$_2$O)$_2$]TiCl$_2$ (**4**) from TiCl$_4$ · 2THF and **1a** in the presence of Et$_3$N

To a solution of $TiCl_4 \cdot 2THF$ (0.75 g, 2.30 mmol) in methylene chloride (30 mL) at −30 °C was added dropwise a solution of **1a** (1.00 g, 2.30 mmol) and Et_3N (0.64 mL, 4.60 mmol) in methylene chloride (30 mL), and the resulting mixture was stirred at the same temperature for 1 h. Then the mixture was heated to room temperature and stirred overnight. The solvent was evaporated under reduced pressure, the crude product was extracted into benzene (2 × 40 mL) and the solution was filtered. After removing of the solvent and recrystallization from a mixture of methylene chloride and heptane, 0.40 g (32%) of compound **4** was obtained, which contains approximately 30% of **3a**.

2.6. Synthesis of [PhN(CH$_2$CH$_2$O)$_2$]Ti(Cl)Cp (**5**)

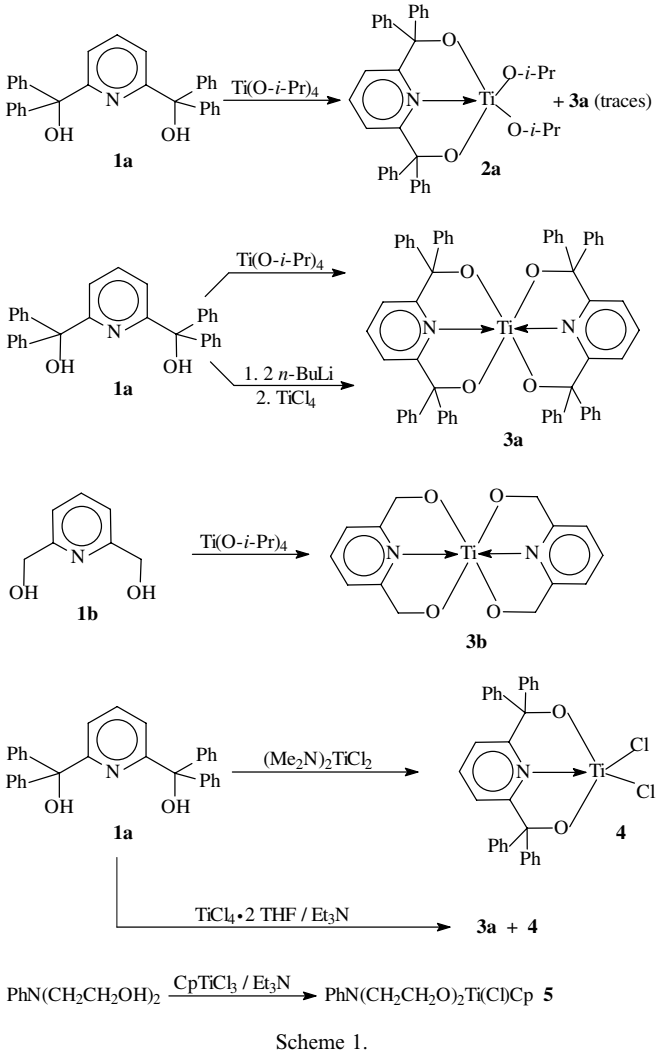
$PhN(CH_2CH_2OH)_2$ (0.54 g, 3.0 mmol) and Et_3N (0.91 g, 9.0 mmol) were added dropwise to a stirred solution of $CpTiCl_3$ (0.66 g, 3.0 mmol) in dichloromethane (50 mL) at −78 °C. The reaction mixture was stirred for 1 h at this temperature and then overnight at room temperature. All volatiles were removed *in vacuo* and the residue was extracted with benzene (2 × 40 mL). The solids were filtered off, the solvent was removed *in vacuo* and then after recrystallization from dichloromethane: *n*-hexane mixture (10:3) 0.56 g (57%) of **5** as a yellow solid was obtained. *Anal.* Calc. for $C_{15}H_{18}NO_2TiCl$: C, 54.99; H, 5.54; N, 4.28. Found: C, 52.60; H, 5.30; N, 4.20%. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 7.32–7.30, 6.82–6.78, 6.73–6.71 (3m, 5H, C_6H_5-group), 6.22 (s, 5H, C_5H_5), 4.87–4.81 (m, 2H, OCH_2), 4.34–4.30 (m, 2H, OCH_2), 3.93–3.89 (m, 2H, NCH_2) 3.28–3.31 (m, 2H, NCH_2). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ (ppm): 147.51, 129.72, 117.44, 111.39 (C_6H_5-group), 116.45 (C_5H_5), 78.98 (OCH_2), 58.15 (NCH_2).

Table 1
Crystal data, data collection and refinement parameters for **3a**

Compound	**3a**
Empirical formula	$C_{69}H_{54}N_2O_4Ti$
Formula weight	1023.04
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.602(4)
b (Å)	14.627(5)
c (Å)	15.874(5)
α (°)	85.735(7)
β (°)	82.715(8)
γ (°)	79.346(15)
V (Å^3)	2622.5(15)
Z	2
D_{calc} (g cm^{-3})	1.296
Absorption coefficient (mm^{-1})	0.218
F(000)	1072
Diffractometer	Bruker SMART 6K
Temperature (K)	120
Radiation λ (Å)	0.71073
θ Range (°)	2.60–28.00
Index ranges	$-15 \leqslant h \leqslant 15$, $-18 \leqslant k \leqslant 19$, $-20 \leqslant l \leqslant 20$
Reflections collected	17812
Independent reflections [R_{int}]	11837 [0.0225]
Data/restraints/parameters	11837/0/858
Goodness-of-fit on F^2	1.049
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0490$; $wR_2 = 0.1179$
R indices (all data)	$R_1 = 0.0652$; $wR_2 = 0.1248$
Largest difference in peak/hole (e Å^{-3})	0.444/−0.413

2.7. X-ray crystallography

Crystal data, data collection, structure solution and refinement parameters for **3a** are listed in Table 1. The structure was solved by direct methods [37] and refined by full matrix least-squares on F^2 [38] with anisotropic thermal parameters for all non-hydrogen atoms (except solvent toluene molecules). Solvent toluene was found to be disordered over two positions with occupancies ratio 0.69/0.31. All hydrogen atoms of the main organometallic molecule were found from diff. Fourier synthesis and refined with isotropic thermal parameters, hydrogen atoms



Scheme 1.

of solvent toluene molecules were placed in calculated positions and refined using a riding model.

3. Results and discussion

3.1. Synthesis of complexes

Our synthetic results are shown in Scheme 1.

According to the literature, compounds of general formula L_2Ti and $LTiX_2$ (where L = dialkanolamine moiety and X = Hal or alkoxy group) are perspective for catalytic investigations [7,14,39,40]. Thus, these derivatives are compounds in question in this report. As we have recently shown, the transalkoxylation reaction is the most suitable route for the preparation of titanocanes and spirobititanocanes [33].

We have found that dialkanolamine **1a** reacted readily with an equimolar amount or 0.5 equiv. of $Ti(O\text{-}i\text{-}Pr)_4$ at reflux temperature in chloroform or toluene solution to give **2a** or **3a** in high yields (Scheme 1). Analogously, unsubstituted analogue of **3a** – compound **3b** – was prepared from **1b** and $Ti(O\text{-}i\text{-}Pr)_4$. The inseparable mixture of **4** and **3a** was found in the reaction of **1a** with $TiCl_4 \cdot 2THF$ in the presence of triethylamine. On the contrary, pure dichloride **5** was obtained in moderate yield from the similar reaction between $PhN(CH_2CH_2OH)_2$ and $CpTiCl_3$.

3.2. NMR spectra

The ^1H NMR spectrum of the prepared Py-containing titanocane **2a** comprises of multiplets of Ph groups and two signals of pyridine group protons as well as two signals of isopropoxy group protons (CH and CH_3). Seven signals of aromatic carbons (four from Ph-groups and three from Py group) as well as two signals of isopropoxy group carbons were found in the ^{13}C NMR spectrum of **2**. Thus, this compound is monomeric in $CDCl_3$ solution at room temperature. It should be noted that all previously prepared diisopropoxytitanocanes are also monomeric in solution [19,33]. The dimerization takes place in the case of non-bulky alkoxy groups (such as methyl) [33]. Also, the equivalence of CPh_2 groups in **4** and CH_2CH_2O arms in **5** allows us to conclude that these compounds are expectedly monomeric in solution at room temperature. According to the NMR spectroscopic data, spirobititanocanes **3a** and **3b** possess a monomeric structure in solution and exist as one geometric isomer.

3.3. Crystal structure

The structure of **3a** was studied by X-ray diffraction (Fig. 1). Table 2 lists selected geometrical parameters for this compound. The monomeric nature of this species with a hexacoordinate titanium center in solid state was confirmed. The coordination polyhedron of the titanium atom represents a distorted octahedron with a rare *trans* disposition (*trans*, *mer* geometry) of the two nitrogen atoms at the Ti atom [33,41,42]. The Ti–N distances in **3a** are very short (2.160(2), 2.161(2) Å). These values are smaller than those previously found in the studied bis(dialkanolamine) derivatives which vary over the range 2.310(2)–2.471(3) Å [33] and in closely related derivatives

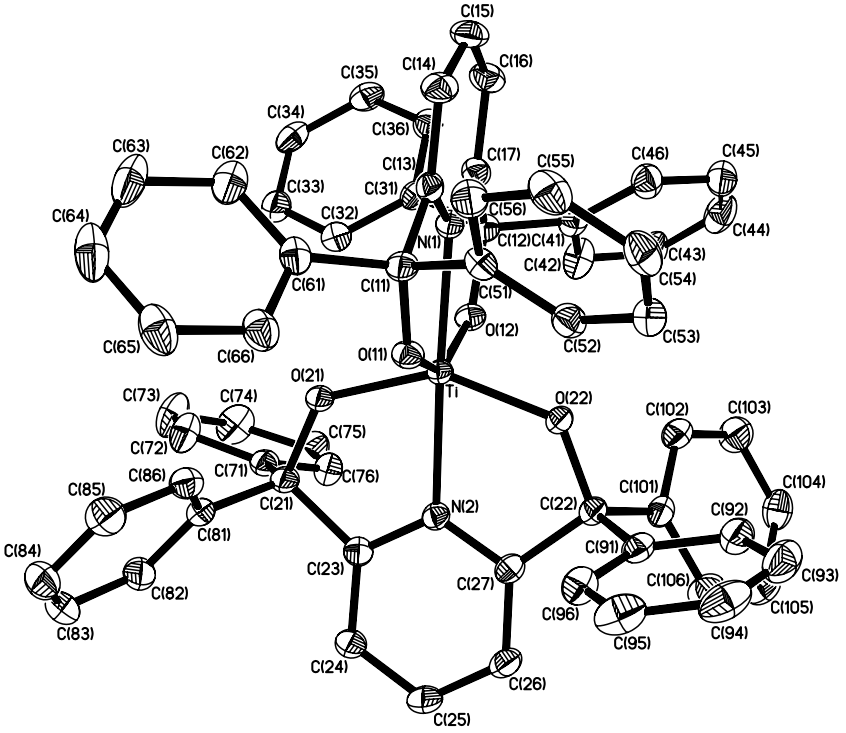


Fig. 1. Molecular structure of **3a**. Hydrogen atoms and toluene molecule are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **3a**

Bond lengths (Å)	
Ti–O(21)	1.884(1)
Ti–O(12)	1.887(1)
Ti–O(22)	1.891(1)
Ti–O(11)	1.898(1)
Ti–N(2)	2.160(2)
Ti–N(1)	2.161(2)
Bond angles (°)	
O(21)–Ti–O(12)	94.82(6)
O(21)–Ti–O(22)	146.48(5)
O(12)–Ti–O(22)	96.73(6)
O(21)–Ti–O(11)	93.99(6)
O(12)–Ti–O(11)	146.61(5)
O(22)–Ti–O(11)	93.42(6)
O(21)–Ti–N(2)	73.62(6)
O(12)–Ti–N(2)	105.58(6)
O(22)–Ti–N(2)	72.99(5)
O(11)–Ti–N(2)	107.81(6)
O(21)–Ti–N(1)	108.25(6)
O(12)–Ti–N(1)	73.06(6)
O(22)–Ti–N(1)	105.21(5)
O(11)–Ti–N(1)	73.58(6)
N(2)–Ti–N(1)	177.69(6)

of pyridine ligands containing one alkoxy arm: $Me_2Ti(Cp^*)$-(OCMePy$_2$), 2.307(3) Å [43], $Cl_2Ti(Cp)[OC(i\text{-}Pr)_2Py]$, 2.254(1) Å [44]. However, these values are close to those previously found in triaza derivatives: {2,6-Py[CH_2N-(2,6-$Me_2C_6H_3$)]$_2$}Ti(Br)CH_2CMe_2Ph, 2.126(6) Å [45]; {2,6-Py[CH_2N(2,6-i-$Pr_2C_6H_3$)]$_2$}Ti[–C($SiMe_3$)=CHC($SiMe_3$)=CH–], 2.172(8) Å [46]. Obviously, the special steric requirements in bis-chelates but not the electronic properties of the substituents around Ti atom cause the shortening of Ti–N_{Py} in **3a**. All atoms of eight-membered ring TiOCCNCCO lie in the same plane. This strictly differs from the tendency previously established for bis(dialknolamine)titanium derivatives where five-membered rings of the ocane skeletons adopt an ''envelope''-like conformation [33]. As we previously found, the shorter Ti–N bonds in the spirobititanocane molecules correspond to longer Ti–O bonds [33]. This tendency is also supported by the structural data for **3a** where Ti–O bond distances are appreciably longer than those in the only X-ray studied monomeric tetraalkoxy titanium derivative with a tetracoordinate Ti atom [1.752(2)–1.825(2) Å] [47].

Thus, we have prepared several titanium complexes based on dihydroxymethylpyridine ligands. The structural investigation showed the strong N_{Py}–Ti interaction in one of them. These compounds may be useful as catalysts in some organic processes where the Lewis acidity of titanium center should be decreased.

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Appendix A. Supplementary material

CCDC 612584 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.10.027.

References

[1] L. Lu, R.A. Johnson, M.G. Finn, K.B. Sharpless, J. Org. Chem. 49 (1984) 728.
[2] S.F. Pedersen, J.C. Dewan, R.R. Eckman, K.B. Sharpless, J. Am. Chem. Soc. 102 (1987) 1279.
[3] B.P. Santora, A.O. Larsen, M.R. Gagne, Organometallics 17 (1998) 3138.
[4] J. Balsells, T.J. Davis, P. Carroll, P.J. Walsh, J. Am. Chem. Soc. 124 (2002) 10336.
[5] K. Mikami, M. Terada, T. Nakai, J. Am. Chem. Soc. 112 (1990) 3949.
[6] S. Piana, I. Devillers, A. Togni, U. Rothlisberger, Angew. Chem. Int. Ed. 41 (2002) 979.
[7] T. Kotsuki, K.B. Sharpless, J. Am. Chem. Soc. 102 (1980) 5974.
[8] B. Stowasser, K.H. Budt, L. Jian-Qi, A. Peynan, D. Ruppert, Tetrahedron Lett. 33 (1992) 6625.
[9] N.J. Hinde, C.D. Hall, J. Chem. Soc., Perkin Trans. 2 (1998) 1249.
[10] V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.
[11] K. Akagi, K. Mochiznki, Y. Aoki, H. Shirakawa, Bull. Chem. Soc. Jpn. 66 (1993) 3444.
[12] Y. Chen, S. Yekta, A.K. Yudir, Chem. Rev. 103 (2003) 3155.
[13] P. Kocovsky, S. Vyskocil, M. Smrcina, Chem. Rev. 103 (2003) 3213.
[14] M. Bonchio, G. Licini, G. Modena, O. Bortolini, S. Moro, W.A. Nugent, J. Am. Chem. Soc. 121 (1999) 6258.
[15] W.A. Nugent, R.L. Harlow, J. Am. Chem. Soc. 116 (1994) 6142.
[16] Y. Kim, G.K. Jnaneshwara, J.G. Verkade, Inorg. Chem. 42 (2003) 1437.
[17] P. Sudhakar, C.V. Amburose, G. Sundararajan, M. Nethaji, Organometallics 23 (2004) 4462.
[18] G. Boche, K. Mobus, K. Harms, M. Marsch, J. Am. Chem. Soc. 118 (1996) 2770.
[19] L. Lavanant, L. Toupet, C.W. Lehmann, J.-F. Carpentier, Organometallics 24 (2005) 5620.
[20] T. Kemmitt, N.I. Al-Salim, G.J. Gainsford, W. Henderson, Aust. J. Chem. 52 (1999) 915.
[21] T. Kemmitt, N.I. Al-Salim, G.J. Gainsford, Aust. J. Chem. 55 (2002) 513.
[22] T. Kemmitt, G.J. Gainsford, N.I. Al-Salim, Acta Cryst. C 60 (2004) m42.
[23] T. Kemmitt, G.J. Gainsford, N.I. Al-Salim, H. Robson-Marsden, D.V. Sevast'yanov, Aust. J. Chem. 56 (2003) 1147.
[24] T. Kemmitt, N.I. Al-Salim, G.J. Gainsford, Eur. J. Inorg. Chem. (1999) 1847.
[25] Y. Kim, H. Han, Y. Do, J. Organomet. Chem. 634 (2001) 19.
[26] R. Manivannan, G. Sundararajan, Macromolecules 35 (2002) 7883.
[27] A.C. Jones, T.J. Leedham, P.J. Wright, M.J. Crosbie, J. Mater. Chem. 11 (2001) 1428.
[28] K.A. Fleeting, D.J. Otway, P. O'Brien, M.E. Pemble, J. Mater. Chem. 8 (1998) 1773.
[29] C. Jimenez, M. Paillous, R. Madar, J.P. Senateur, A.C. Jones, J. Phys. IV Fr. 9 (1999) 568.
[30] J.-H. Lee, J.-Y. Kim, J.-Y. Shim, S.-W. Rhee, J. Vac. Sci. Technol. A 17 (1999) 3033.

[31] J. Hawkins, K.B. Sharpless, Tetrahedron Lett. 28 (1987) 2825.
[32] K.V. Zaitsev, S.S. Karlov, M.V. Zabalov, A.V. Churakov, G.S. Zaitseva, D.A. Lemenovskii, Russ. Chem. Bull., Int. Ed. 54 (2006) 2831.
[33] K.V. Zaitsev, S.S. Karlov, A.A. Selina, Yu.F. Oprunenko, A.V. Churakov, B. Neumüller, J.A.K. Howard, G.S. Zaitseva, Eur. J. Inorg. Chem. (2006) 1987.
[34] E. Gomez, V. Santes, V. Luz, N. Farfan, J. Organomet. Chem. 622 (2001) 54.
[35] E. Benzing, W. Kornicker, Chem. Ber. 94 (1961) 142.
[36] A.M. Cardoso, R.J.H. Clark, S. Moorhouse, J. Chem. Soc., Dalton Trans. (1980) 1156.
[37] G.M. Sheldrick, Acta Cryst. A 46 (1990) 467.
[38] G.M. Sheldrick, Program for the Refinement of Crystal Structures, SHELXL-97, University of Göttingen, Germany.
[39] H.B. KaganComprehensive Organic Chemistry, vol. 8, Pergamon, Oxford, 1992.
[40] M.C.W. Chan, K.-H. Tam, Y.-L. Pui, N. Zhu, J. Chem. Soc., Dalton Trans. (2002) 3085.
[41] A. Caneschi, A. Dei, D. Gatteschi, J. Chem. Soc., Chem. Commun. (1992) 630.
[42] H. Hefele, E. Ludwig, E. Uhleman, H. Nöth, Z. Anorg. Allg. Chem. 621 (1995) 1431.
[43] R. Fandos, C. Hernández, A. Otero, A.M. Rodríguez, M.J. Ruiz, P. Terreros, J. Chem. Soc., Dalton Trans. (2000) 2990.
[44] S. Doherty, R.J. Errington, A.P. Jarvis, S. Collins, W. Clegg, M.R.J. Elsegood, Organometallics 17 (1998) 3408.
[45] F. Guérin, D.H. McConville, N.C. Payne, Organometallics 15 (1996) 5085.
[46] F. Guérin, D.H. McConville, J.J. Vittal, Organometallics 16 (1997) 1491.
[47] S.M. Damo, K.-C. Lam, A. Rheingold, M.A. Walters, Inorg. Chem. 39 (2000) 1635.