Inorg. Chem. **1992**, *31*, 4933–4938 **4933**

Linear Trimeric, Dimeric, and Monomeric Titanium(III) Aryloxides†

Ravinder Minhas, Robbert Duchateau, Sandro Gambarotta,* and Corinne Bensimon

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Received February 28, 1992

Reactions of *trans*-Ti(TMEDA)$_2$Cl$_2$ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) with 2 equiv of RONa [R = Ph, 3,5-(t-Bu)$_2$C$_6$H$_3$] formed the paramagnetic light-green linear trimeric Ti(III) derivative Ti$_3$(PhO)$_9$(TMEDA)$_2$ (**1**) and the pink dimeric complex [Ti(RO)Cl(TMEDA)]$_2$(μ-OR)$_2$ [R = 3,5-(t-Bu)$_2$C$_6$H$_3$] (**2**), respectively. Complex **1** could also be conveniently synthesized from TiCl$_3$(THF)$_3$ and PhONa in the presence of TMEDA. Conversely, complex **2** could be obtained from TiCl$_3$(THF)$_3$ only when the reaction was carried out in toluene, since bright-yellow crystals of the mononuclear anionic complexes [Ti(RO)$_2$(TMEDA)Cl$_2$][M′] [M′ = Na(TMEDA)$_2^+$ (**3a**), $^1/_2$(TMEDA)H$^+$ (**3b**)] were isolated when the reaction was performed in THF. Reaction of Ti[N(SiMe$_3$)$_2$]$_3$ with 3 equiv of 2,6-Me$_2$C$_6$H$_3$OH in toluene led to the formation of the first dinuclear homoleptic complex [Ti(RO)$_3$]$_2$ [R = 2,6-Me$_2$C$_6$H$_3$ (**4**)], which was isolated as green-blue crystals. A similar reaction with the more bulky 2,6-(i-Pr)$_2$C$_6$H$_3$OH led to the formation of the neutral homoleptic Ti(IV) species Ti[OC$_6$H$_3$-2,6-(i-Pr)$_2$]$_4$ (**6**). Conversely, the anionic homoleptic complex {Ti[OC$_6$H$_3$-2,6-(i-Pr)$_2$]$_4$}{Li(TMEDA)$_2$}·toluene (**7**) was obtained by reacting the corresponding lithium phenoxide with TiCl$_3$(THF)$_3$. The structures of **1**, **3b**, and **4** were determined by X-ray analysis. Crystal data are as follows. **1**: monoclinic, $C2/c$, a = 14.758 (5) Å, b = 21.920 (2) Å, c = 11.855 (1) Å, β = 102.339 (4)°, V = 6274 (7) Å^3, Z = 4, R = 0.058 (R_w = 0.024) for 417 parameters and 2425 significant reflections out of 4648. **3b**: triclinic, $P\bar{1}$, a = 12.877 (2) Å, b = 16.850 (3) Å, c = 12.605 (2) Å, α = 106.65 (1)°, β = 100.65 (1)°, γ = 68.63 (1)°, V = 2430.4 (7) Å^3, Z = 2, R = 0.080 (R_w = 0.081) for 435 parameters and 4685 significant reflections out of 7234. **4**: triclinic, $P\bar{1}$, a = 11.372 (3) Å, b = 11.458 (3) Å, c = 10.859 (4) Å, α = 117.04 (2)°, β = 115.29 (3)°, γ = 93.56 (4)°, V = 1080.1 (9) Å^3, Z = 2, R = 0.036 (R_w = 0.051) for 362 parameters and 3297 significant reflections out of 4020.

Introduction

Interest in the chemistry of low-valent titanium has been stimulated by some remarkable performances reported for these systems, including catalytic dinitrogen activation/fixation[1] and the enormous reducing capability of these species with the large majority of organic substrates.[2] Among the possible supporting ligands, alkoxides and aryloxides seem particularly versatile due to (i) the unlimited choice of organic substituents, which allows fine tuning of the steric hindrance around the transition metal, (ii) the electronic flexibility of the oxygen donor atom, which allows different molecular complexities by adopting several bonding modes, and (iii) the possibility of readily introducing optical activity by using largely available optically active alkoxides. In line with these great expectations, Rothwell has shown in a recent series of papers that several attractive transformations (reductive couplings,[3] oxidative additions,[4] formation of imide,[5] and ethylene coordination[6]) can be performed with in situ generated low-valent titanium aryloxides. Despite these promising features, low-valent titanium aryloxides are surprisingly scarce.[7] Only two examples of monomeric Ti(II) aryloxides with strongly stabilizing ligands (dmpe,[8] bpy[9]), one dimeric Ti(III) aryloxide halide with an intriguingly short Ti–Ti nonbonding distance,[10] one monomeric aryloxide dihalide,[11] and two tricoordinated homoleptic derivatives, whose structures remain unknown, have been reported to date.[12] The possibility of stabilizing low-valent

---

† In memory of Prof. J. L. Roustan.

(1) (a) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358. (b) Van Tamelen, E. E. *Acc. Chem. Res.* **1970**, *3*, 361. (c) Flamini, A.; Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 454. (d) Sobota, P.; Janas, Z. *Inorg. Chim. Acta* **1981**, *53*, L11. (e) Berry, D. H.; Procopio, L. J.; Carroll, P. J. *Organometallics* **1988**, *7*, 570. (f) Volpin, M. E.; Shur, V. B.; Kudryavtsev, R. V.; Prodayko, L. A. *J. Chem. Soc., Chem. Commun.* **1968**, 1038. (g) Duchateau, R.; Gambarotta, S.; Beydhoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986. (h) Beydhoun, N.; Duchateau, R.; Gambarotta, S. *J. Chem. Soc., Chem. Commun.* **1992**, 244.

(2) (a) Alt, H. G.; Schwind, K. H.; Rausch, M. D. *J. Organomet. Chem.* **1987**, *321*, C9. (b) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. (c) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (d) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376. (e) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Am. Chem. Soc.* **1985**, *107*, 3717. (f) Famili, A.; Farona, M. F.; Thanedar, S. *J. Chem. Soc., Chem. Commun.* **1983**, 435. (g) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. Boor, J. *Ziegler-Natta Catalysts and Polymerization*, Academic Press: New York, 1979. (i) Duchateau, R.; Williams, A. J.; Gambarotta, S.; Chiang, M. Y. *Inorg. Chem.* **1991**, *30*, 4863.

(3) (a) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1775. (b) Hill, J. E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 3428. (c) Hill, J. E.; Fanwick, G. J.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211. (d) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Lateski, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068. (e) Durfee, L. D.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 1463.

(4) (a) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720. (b) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75. (c) Lateski, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981.

(5) (a) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (b) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1991**, *30*, 1143.

(6) (a) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771. (b) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1775.

(7) Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982.

(8) (a) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339. (b) Jensen, J. A.; Wilson, S. R.; Schultz, A. J.; Girolami, G. S. *J. Am. Chem. Soc.* **1987**, *109*, 8094. (c) Gardner, T. G.; Girolami, G. S. *Organometallics* **1987**, *6*, 2551. (d) Morris, R. J.; Girolami, G. S. *Inorg. Chem.* **1990**, *29*, 4167.

(9) (a) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720. (b) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75.

(10) Hill, J. E.; Nash, J. M.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 1617.

(11) Mazzanti, M.; Floriani, C.; Guastini, C.; Chiesi-Villa, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1793.

0020-1669/92/1331-4933$03.00/0

titanium highly-reactive functionalities (hydrides and alkyls), using alkoxides as supporting ligands, remains unexplored.

Our interest in the chemistry of low-valent titanium aryloxides is mainly focused on two general characteristics. The ability of aryloxides to bridge two or more metal centers, which is a prerequisite for the occurrence of short Ti–Ti contacts, makes these compounds promising substrates for studying the nature of the magnetic couplings between titanium(II) and -(III) atoms (magnetic exchange, metal–metal bond, etc). It should be noted that metal–metal bonds between d^1 and d^2 titanium atoms are surprisingly rare.[13] The second characteristic of interest is the very high reducing power of low-valent titanium, which might allow the preparation of high-nuclearity mixed-valence or high-valent titanium oxide and sulfide aggregates via facile oxidation reactions with either O$_2$ or S$_8$.

In this preliminary paper, we describe the synthesis and characterization of some trivalent titanium aryloxides obtained from ligand-replacement reactions of Ti(II) and Ti(III) halides.

Experimental Section

All operations were performed under inert atmosphere (N$_2$ or Ar) using standard Schlenk techniques or in a nitrogen-filled drybox (Vacuum Atmospheres); TiCl$_2$(TMEDA)$_2$ (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) and TiCl$_3$(THF)$_3$ were prepared according to published procedures.[14] TMEDA was chromatographed over Al$_2$O$_3$ and distilled over molten potassium, after refluxing; pyridine was refluxed over CaH$_2$ and distilled under nitrogen using a Vigreux column; phenols (Aldrich) were purified by sublimation. The NaH suspension in mineral oil was washed with hexane, dried, and stored under nitrogen in sealed ampules. Infrared spectra were recorded on a Perkin-Elmer 393 instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out at the Microanalytical Section of the Chemistry Department, Rijksuniversiteit Groningen, and at Galbraith Laboratories. Samples for magnetic susceptibility measurements were sealed in calibrated tubes inside a drybox. Measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods,[15] and corrections for underlying diamagnetism were applied to the data.[16]

Preparation of Ti$_3$(PhO)$_9$(TMEDA)$_2$ (1). A solution of phenol (1.7 g, 18.1 mmol) in THF (75 mL) was stirred and refluxed with NaH (0.45 g, 18.8 mmol) for 30 min and then filtered; the filtrate was cooled to −90 °C. The addition of *trans*-(TMEDA)$_2$TiCl$_2$ (3.1 g, 10.5 mmol) caused slow formation of a red color. The mixture was stirred and allowed to warm slowly to ambient temperature (3 h). The resulting red solution was evaporated in vacuo and the residual red solid suspended in toluene (75 mL). The resulting suspension was filtered, and the filtrate was then concentrated to a small volume (20 mL). Light-green crystals of **1** (1.7 g, 1.4 mmol, 40%) separated from the mixture upon cooling to −30 °C. Anal. Calcd (found) for C$_{66}$H$_{77}$O$_9$N$_4$Ti$_3$: C, 65.30 (65.27); H, 6.39 (6.28); N, 4.26 (4.17); Ti, 11.83 (11.07). $\mu_{\rm eff} = 1.69\ \mu_{\rm B}$.

Preparation of [Ti(OR)Cl(TMEDA)]$_2$(μ-OR)$_2$ [R = 3,5-(*t*-Bu)$_2$C$_6$H$_3$] (2). A solution of 3,5-(*t*-Bu)$_2$PhOH (4.5 g, 21.8 mmol) in THF (60 mL) was stirred and refluxed with NaH (0.6 g, 25.0 mmol) for 30 min and then cooled to −90 °C. The addition of *trans*-(TMEDA)$_2$TiCl$_2$ (3.7 g, 12.5 mmol) caused slow formation of a deep-orange color. The mixture was stirred and allowed to warm slowly to ambient temperature (3 h). The resulting deep-orange-brown solution was evaporated in vacuo and the residual red solid suspended in toluene (75 mL). The suspension was filtered, and the filtrate was concentrated to a small volume (20 mL). Light-pink crystals of **2** (2.9 g, 2.5 mmol, 40%) separated from the mixture upon slow concentration. Anal. Calcd (found) for C$_{68}$H$_{70}$O$_4$N$_4$Cl$_2$Ti$_2$: C, 69.57 (69.37); H, 6.01 (5.88); N, 4.77 (4.51); Ti, 8.16 (8.01). $\mu_{\rm eff} = 0.75\ \mu_{\rm B}$.

Preparation of [Ti(OR)$_2$(TMEDA)Cl$_2$][Na(TMEDA)$_2$(THF)] [R = 3,5-(*t*-Bu)$_2$C$_6$H$_3$] (3a). A THF solution (75 mL) of freshly sublimed 3,5-(*t*-Bu)$_2$C$_6$H$_3$OH (3.2 g, 15 mmol) was refluxed and stirred with NaH (0.5 g, 20 mmol). Excess NaH was filtered off, and the resulting clear solution was added to a solution of TiCl$_3$(THF)$_3$ (2.8 g, 7.7 mmol) in THF (50 mL) containing TMEDA (4 mL). The resulting orange mixture was evaporated to dryness and the residual solid suspended in toluene (50 mL). The mixture was filtered, concentrated to a small volume (30 mL), and layered with hexane (30 mL). Orange-red crystals of **3a** (2.6 g, 2.8 mmol, 37%) separated from the mixture upon standing overnight at −30 °C. Anal. Calcd (found) for C$_{50}$H$_{98}$O$_3$N$_6$Cl$_2$TiNa: C, 61.71 (61.37); H, 10.15 (10.08); N, 8.64 (8.51); Ti, 4.92 (4.51). $\mu_{\rm eff} = 1.79\ \mu_{\rm B}$.

Preparation of [Ti(OR)$_2$(TMEDA)Cl$_2$][(TMEDA)H]$_{0.5}$ [R = 3,5-(*t*-Bu)$_2$C$_6$H$_3$] (3b). A solution of 3,5-(*t*-Bu)$_2$PhOH (4.5 g, 21.8 mmol) in THF (130 mL) was stirred and refluxed with NaH (0.8 g, 33.3 mmol) for 30 min. The addition of a solution of TiCl$_3$(THF)$_3$ (4.0 g, 10.8 mmol) in THF (100 mL), containing a small amount of TMEDA (2.5 mL), caused slow formation of an orange-yellow color. The mixture was stirred for 2 h at ambient temperature. The resulting orange-yellow suspension was evaporated in vacuo and the residual yellow solid suspended in toluene (150 mL). The suspension was filtered, and the filtrate was concentrated to a small volume (20 mL). Bright-yellow crystals of **3b** (1.2 g, 1.5 mmol, 14%) separated from the mixture upon cooling to −30 °C. Anal. Calcd (found) for C$_{44}$H$_{74}$O$_2$N$_3$Cl$_2$Ti: C, 66.40 (66.79); H, 9.37 (8.66); N, 5.28 (5.22); Ti, 6.02 (5.99). $\mu_{\rm efr} = 1.93\ \mu_{\rm B}$.

Preparation of [Ti(2,6-Me$_2$C$_6$H$_3$O)$_3$]$_2$ (4). A deep-blue-violet solution of [(Me$_3$Si)$_2$N]$_3$Ti (5.0 g, 9.4 mmol) in toluene (70 mL) was treated with freshly sublimed 2,6-Me$_2$PhOH (3.5 g, 28.6 mmol). The mixture was refluxed 2 h, upon which the color turned green-blue. The solution was concentrated and layered with hexane. Green-blue crystals of **4** were obtained upon standing overnight at room temperature (3.7 g, 4.5 mmol, 96%). Anal. Calcd (found) for C$_{48}$H$_{54}$O$_6$Ti$_2$: C, 70.08 (69.99); H, 6.62 (6.55); Ti, 11.64 (11.11). $\mu_{\rm eff} = 0.64\ \mu_{\rm B}$.

Preparation of Ti[N(SiMe$_3$)$_2$]$_3$ (5). A suspension of TiCl$_3$(THF)$_3$ (15.0 g, 40 mmol) in toluene (300 mL) was treated with (Me$_3$Si)$_2$NLi (20.3 g, 120 mmol). The mixture was stirred and boiled for a few minutes and filtered while hot. Purple crystals of **5** (14.8 g, 29 mmol, 73%) separated from the resulting purple solution upon standing overnight at −30 °C. Anal. Calcd (found) for C$_{18}$H$_{54}$Si$_6$N$_3$Ti: C, 40.87 (40.02); H, 10.29 (10.11); N, 7.94 (7.33); Ti, 9.05 (8.87). $\mu_{\rm eff} = 1.74\ \mu_{\rm B}$.

Preparation of Ti[2,6-(*i*-Pr)$_2$C$_6$H$_3$O]$_4$ (6). The addition of 2,6-(*i*-Pr)$_2$C$_6$H$_3$OH (3.0 g, 17 mmol) to a purple solution of **5** (3.0 g, 5.7 mmol) in toluene (50 mL) turned the color deep orange. The solution was concentrated to a small volume (30 mL) and layered with hexane (50 mL) in a round-bottomed flask. Bright-yellow air-stable crystals of **6** (1.9 g, 2.5 mmol, 45%) were obtained upon standing 2 days at room temperature. Anal. Calcd (found) for C$_{48}$H$_{68}$O$_4$Ti: C, 76.16 (75.99); H, 9.06 (8.86); Ti, 6.33 (6.00). The compound is diamagnetic.

Preparation of {Ti[2,6-(*i*-Pr)$_2$C$_6$H$_3$O]$_4$}[(TMEDA)$_2$Li]·C$_7$H$_8$ (7). A solution of MeLi in ether (31 mL, 1.4 M) was added dropwise to a solution of 2,6-(*i*-Pr)$_2$C$_6$H$_3$OH (8 mL, 43.2 mmol) in THF (150 mL) cooled to −80 °C. After the mixture was warmed to room temperature and further cooled to −80 °C, neat TMEDA (4.0 mL, 26.5 mmol) and TiCl$_3$(THF)$_3$ (4.0 g, 10.8 mmol) were added. The resulting emerald-green slurry was stirred during the warming period and for additional 2 h at room temperature. The solvent was evaporated in vacuo and the residual solid redissolved in toluene (100 mL). After filtration and concentration, orange crystals of **7** (7.5 g, 6.9 mmol, 64%) separated from the resulting blue-green solution upon standing at −30 °C overnight. Anal. Calcd (found) for C$_{67}$H$_{108}$O$_4$N$_4$TiLi: C, 73.93 (73.69); H, 10.00 (9.86); N, 5.15 (5.01); Ti, 4.40 (4.17). $\mu_{\rm eff} = 1.67\ \mu_{\rm B}$.

X-ray Crystallography. Data were collected at room temperature for complexes **1** and **3b** and at −160 °C for **4**. The ω-2θ scan technique (maximum 2θ 50.0°) was used for suitable air-sensitive crystals sealed in a glass capillary for room-temperature measurements or mounted on a glass fiber for low-temperature measurements. Cell constants and orientation matrixes were obtained from the least-squares refinement of 25 carefully centered reflections in maximum ranges of $40° < 2\theta < 50°$, $40° < 2\theta < 47°$, and $40° < 2\theta < 43.9°$ for **1**, **3b**, and **4**, respectively. The intensities of three representative reflections measured after every 150 reflections indicated crystal and electronic stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures

---

(12) (a) Covert, J. K.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J. *Inorg. Chem.* **1992**, *31*, 66. (b) Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995.

(13) (a) Edema, J. J. H.; Duchateau, R.; Gambarotta, S.; Bensimon, C. *Inorg. Chem.* **1991**, *30*, 3585. (b) Schafer, H.; Laumanns, R.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 325. (c) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 7870. (d) Gauvin, F.; Britten, J.; Samuel, E.; Harrod, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 1489.

(14) Edema, J. J. H.; Duchateau, R.; Gambarotta, S.; Hynes, R.; Gabe, E. *Inorg. Chem.* **1991**, *30*, 154.

(15) Mabbs, M. B.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

(16) Foese, G.; Gorter, C. J.; Smits, L. J. *Constantes Selectionnées Diamagnetisme, Paramagnetisme, Relaxation Paramagnetique*; Masson: Paris, 1957.

Table I. Crystal Data and Structural Analysis Results

complex	**1**	**3b**	**4**
formula	$C_{66}H_{77}N_4O_9Ti_3$	$C_{44}H_{74}N_3O_2Cl_2Ti$	$C_{24}H_{27}O_3Ti$
fw	1214.04	798.88	411.38
crystal system	monoclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	14.758 (5)	12.877 (2)	11.373 (3)
b (Å)	21.920 (17)	16.850 (3)	11.458 (3)
c (Å)	19.855 (13)	12.605 (2)	10.859 (4)
α (deg)		106.65 (1)	117.04 (2)
β (deg)	102.339 (4)	100.65 (1)	115.29 (3)
γ (deg)		68.63 (1)	93.56 (4)
V (Å^3)	6274 (7)	2430.4 (7)	1080.1 (9)
Z	4	2	2
radiation: λ(Mo Kα) (Å)	0.709 30	0.709 30	0.710 69
T (°C)	25	25	-158
D_{calcd} (g cm^{-3})	1.285	1.078	1.265
μ_{calcd} (cm^{-1})	4.0	3.1	4.10
R, R_w	0.058, 0.024	0.080, 0.081	0.036, 0.051

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **1**

	x	y	z	U_{eq}[a] (Å^2)
Ti1	0.0000	0.30845 (7)	0.2500	2.85 (8)
Ti2	0.11388 (8)	0.34457 (5)	0.13171 (5)	3.12 (6)
O1	0.13145 (22)	0.32848 (16)	0.23698 (17)	3.22 (20)
O2	–0.01803 (22)	0.34771 (17)	0.15589 (16)	3.48 (20)
O3	0.1021 (3)	0.26090 (17)	0.10825 (18)	4.24 (22)
O4	0.1351 (3)	0.42910 (16)	0.14193 (18)	3.99 (22)
O5	0.0000	0.22671 (24)	0.2500	4.6 (4)
N1	0.0862 (3)	0.36822 (22)	0.01162 (21)	4.0 (3)
N2	0.2652 (3)	0.33927 (23)	0.11074 (21)	4.2 (3)
C1	0.21740 (18)	0.32308 (20)	0.28015 (14)	3.2 (3)
C2	0.2740 (3)	0.37429 (13)	0.29609 (18)	3.8 (3)
C3	0.3634 (3)	0.36818 (17)	0.33640 (19)	4.9 (4)
C4	0.30609 (18)	0.31086 (23)	0.36077 (15)	5.3 (4)
C5	0.3395 (3)	0.25965 (15)	0.34483 (20)	5.4 (4)
C6	0.2501 (3)	0.26575 (15)	0.30452 (20)	4.0 (3)
C7	–0.09600 (19)	0.36567 (21)	0.10927 (15)	3.5 (3)
C8	–0.1218 (3)	0.42701 (18)	0.10436 (18)	4.2 (4)
C9	–0.2011 (3)	0.44523 (17)	0.05698 (24)	6.0 (4)
C10	–0.25477 (21)	0.4021 (3)	0.01449 (17)	7.4 (5)
C11	–0.2290 (3)	0.34076 (24)	0.01940 (17)	6.4 (4)
C12	0.1496 (3)	0.32255 (14)	0.06679 (23)	5.1 (4)
C13	0.0927 (3)	0.19961 (13)	0.09651 (22)	3.6 (3)
C14	0.15456 (22)	0.15939 (22)	0.13714 (14)	4.8 (4)
C15	0.1485 (3)	0.09594 (20)	0.12335 (20)	5.0 (4)
C16	0.0806 (3)	0.07472 (13)	0.06893 (24)	5.5 (4)
C17	0.01879 (23)	0.11494 (22)	0.02830 (15)	5.4 (4)
C18	0.02483 (23)	0.17738 (20)	0.04209 (18)	4.9 (4)
C19	0.1401 (3)	0.48536 (13)	0.16820 (21)	3.5 (3)
C20	0.1766 (3)	0.53278 (21)	0.13534 (14)	5.2 (4)
C21	0.1821 (3)	0.59153 (17)	0.16291 (22)	6.1 (4)
C22	0.1510 (3)	0.60288 (14)	0.22333 (23)	6.5 (5)
C23	0.1145 (3)	0.55547 (22)	0.25619 (15)	6.5 (5)
C24	0.1091 (3)	0.4967 (17)	0.22863 (21)	4.7 (4)
C25	0.0000	0.1647 (4)	0.250000	3.8 (5)
C26	–0.0578 (4)	0.1314 (3)	0.1994 (3)	5.8 (4)
C27	–0.0571 (5)	0.0702 (3)	0.2012 (3)	8.1 (5)
C28	0.0000	0.0374 (4)	0.2500	9.1 (9)
C29	0.1796 (4)	0.3793 (3)	–0.0018 (3)	5.4 (4)
C30	0.2505 (4)	0.3346 (3)	0.0355 (3)	6.0 (4)
C31	0.3191 (4)	0.2854 (3)	0.1415 (3)	5.8 (5)
C32	0.3269 (4)	0.3822 (3)	0.1335 (3)	6.2 (4)
C33	0.0320 (4)	0.4245 (3)	–0.0073 (3)	5.4 (4)
C34	0.0407 (4)	0.3194 (3)	–0.0340 (3)	5.9 (4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_ia_j\mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **3b**

	x	y	z	U_{eq}[a] (Å^2)
Ti	0.25800 (12)	0.93892 (9)	0.29744 (11)	3.49 (7)
Cl1	0.29534 (16)	0.92007 (12)	0.10311 (15)	4.38 (11)
Cl2	0.06490 (18)	1.04204 (14)	0.28420 (18)	5.97 (14)
O1	0.3175 (4)	1.0326 (3)	0.3471 (4)	4.1 (3)
O2	0.2083 (4)	0.8407 (3)	0.2509 (4)	4.8 (3)
N1	0.2474 (5)	0.9451 (4)	0.4790 (4)	5.3 (4)
N2	0.4369 (5)	0.8471 (14)	0.3389 (5)	5.0 (4)
N3	0.0939 (5)	1.0701 (4)	0.0356 (5)	5.7 (4)
C1	0.3173 (6)	1.1061 (4)	0.3258 (5)	3.5 (4)
C2	0.2517 (6)	1.1862 (4)	0.3812 (5)	4.0 (4)
C3	0.2508 (6)	1.2639 (4)	0.3621 (5)	4.2 (4)
C4	0.3187 (6)	1.2591 (4)	0.2848 (6)	4.4 (5)
C5	0.3845 (6)	1.1791 (4)	0.2260 (5)	3.9 (4)
C6	0.3838 (6)	1.1025 (4)	0.2484 (5)	3.7 (4)
C7	0.5429 (6)	0.8272 (5)	–0.1375 (5)	4.5 (5)
C8	0.4207 (6)	0.8782 (5)	–0.1678 (6)	6.1 (6)
C9	0.5835 (6)	0.8766 (5)	–0.0243 (6)	5.5 (5)
C10	0.5489 (7)	0.7390 (5)	–0.1245 (6)	6.4 (6)
C11	0.1782 (7)	1.3537 (5)	0.4241 (7)	7.1 (6)
C12	0.1540 (14)	1.4212 (6)	0.3717 (12)	26.4 (12)
C13	0.0711 (11)	1.3514 (7)	0.4347 (13)	21.6 (14)
C14	0.2182 (13)	1.3776 (8)	0.5315 (10)	28.3 (13)
C15	0.1707 (6)	0.7787 (4)	0.1800 (6)	4.3 (5)
C16	0.0762 (6)	0.7645 (4)	0.1995 (5)	3.9 (4)
C17	0.0399 (6)	0.6971 (4)	0.1288 (6)	4.1 (4)
C18	0.1007 (6)	0.6444 (4)	0.0394 (6)	4.6 (5)
C19	0.1940 (6)	0.6586 (4)	0.0156 (6)	4.6 (5)
C20	0.2281 (6)	0.7255 (4)	0.0858 (5)	4.3 (4)
C21	–0.0615 (6)	0.6789 (5)	0.1498 (6)	5.1 (5)
C22	–0.1308 (8)	0.7518 (6)	0.2368 (8)	9.0 (8)
C23	–0.0207 (7)	0.5945 (5)	0.1893 (7)	7.6 (7)
C24	–0.1385 (7)	0.6671 (6)	0.0432 (7)	7.6 (7)
C25	0.2601 (7)	0.5998 (5)	–0.0833 (6)	6.8 (6)
C26	0.3063 (11)	0.5056 (7)	–0.0691 (10)	16.1 (11)
C27	0.3529 (11)	0.6227 (8)	–0.0962 (10)	19.1 (13)
C28	0.1876 (10)	0.5923 (9)	–0.1835 (8)	17.6 (12)
C29	0.3594 (9)	0.8961 (7)	0.5179 (7)	11.8 (9)
C30	0.4346 (9)	0.8445 (7)	0.4520 (7)	12.5 (9)
C31	0.1632 (8)	0.9088 (6)	0.4907 (6)	8.9 (8)
C32	0.2192 (8)	1.0338 (5)	0.5499 (6)	7.6 (7)
C33	0.4648 (8)	0.7577 (5)	0.2673 (8)	9.2 (7)
C34	0.5263 (7)	0.8793 (5)	0.3333 (8)	8.7 (7)
C35	–0.0110 (6)	1.0493 (4)	0.0154 (7)	4.9 (5)
C36	0.1397 (7)	1.0540 (6)	–0.0712 (7)	7.7 (7)
C37	0.0785 (8)	1.1614 (5)	0.0991 (7)	7.2 (6)
C38	0.3202 (9)	0.6009 (7)	0.3742 (9)	12.2 (4)
C39	0.2315 (9)	0.6431 (7)	0.4244 (9)	11.7 (4)
C40	0.2035 (10)	0.6924 (8)	0.5410 (10)	14.4 (4)
C41	0.3220 (10)	0.6806 (7)	0.5964 (9)	13.1 (4)
C42	0.4139 (9)	0.6329 (7)	0.5317 (8)	11.4 (4)
C43	0.4538 (11)	0.5861 (8)	0.4218 (10)	15.8 (5)
C44	0.3669 (12)	0.5220 (9)	0.2730 (11)	18.2 (5)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_ia_j\mathbf{a}_i\cdot\mathbf{a}_j$.

were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated but not refined. In the case of complex **4**, hydrogen atoms were located in difference Fourier maps and their positions refined isotropically with one common thermal parameter. The final cycles of full-matrix least-squares refinement were based on the number of observed reflections with $I > 2.5\sigma(I)$ and corresponding parameters. Anomalous dispersion effects were included in F_c. All calculations were performed using the TEXSAN and NRCVAX packages on a Digital VAX station. Details on data collections and structure refinements are reported in Table I and as supplementary material. The final atomic coordinates are given in Tables II–IV. Selected bond distances and angles are given in Table V.

Results

As illustrated in Scheme I, the reactions of *trans*-Ti(TMEDA)$_2$Cl$_2$[14] with 2 equiv of the appropriate sodium aryloxide were carried out in THF at -80 °C. The resulting deep-red-orange solutions, obtained after warming to room temperature, were evaporated, and very air-sensitive crystalline samples were obtained by crystallization of the residual solids from toluene at -30 °C (Scheme I). The nuclearity of these complexes seems to be dependent on both the presence of substituents on the aromatic ring and the utilization of coordinating solvents. The linear trimeric structure of [Ti(TMEDA)(PhO)$_2$]$_2$[Ti(PhO)](μ-OPh)$_4$ (**1**), which was prepared as light-green, air-sensitive crystals in the case of PhONa, is in fact disrupted by THF, forming Ti(PhO)$_3$(TMEDA)(THF) as a bright-yellow solid. While the reaction could be reversed by treating the yellow compound in

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **4**

	x	y	z	$U_{eq}{}^a$ (Å^2)
Ti1	0.10871 (4)	0.14133 (4)	0.09112 (5)	1.43 (1)
O1	0.1214 (2)	0.2879 (2)	0.2688 (2)	2.04 (5)
O2	0.2140 (2)	0.1686 (2)	0.0127 (2)	1.90 (5)
O3	−0.0846 (2)	0.0319 (2)	−0.0938 (2)	1.61 (4)
C1	0.2589 (2)	0.2264 (2)	−0.0517 (3)	1.69 (5)
C2	0.3286 (2)	0.1618 (2)	−0.1283 (3)	1.79 (6)
C3	0.3744 (3)	0.2220 (3)	−0.1927 (3)	2.44 (8)
C4	0.3528 (3)	0.3439 (3)	−0.1785 (3)	2.85 (8)
C5	0.2822 (3)	0.4047 (3)	−0.1042 (3)	2.58 (8)
C6	0.2331 (3)	0.3480 (2)	−0.0393 (3)	2.05 (7)
C7	0.1546 (3)	0.4124 (3)	0.0401 (4)	2.9 (1)
C8	0.3511 (3)	0.0302 (3)	0.1416 (3)	2.24 (7)
C9	0.2037 (3)	0.4119 (2)	0.4088 (3)	1.87 (7)
C10	0.1531 (3)	0.5235 (3)	0.4441 (3)	2.42 (7)
C11	−0.2388 (4)	0.6471 (3)	0.5893 (3)	3.2 (1)
C12	0.3692 (4)	0.6610 (3)	0.6960 (3)	3.7 (1)
C13	0.4177 (3)	0.5502 (3)	0.6566 (3)	3.14 (9)
C14	0.3368 (3)	0.4237 (3)	0.5127 (3)	2.28 (7)
C15	0.3895 (3)	0.3030 (3)	0.4700 (4)	3.0 (1)
C16	0.0121 (4)	0.5107 (4)	0.3296 (4)	3.4 (1)
C17	−0.1577 (2)	0.0757 (2)	−0.1962 (3)	1.60 (6)
C18	−0.1414 (2)	0.0441 (2)	−0.3274 (3)	1.90 (7)
C19	−0.2071 (3)	0.0996 (3)	−0.4181 (3)	2.61 (8)
C20	−0.2875 (3)	0.1792 (3)	−0.3830 (4)	3.1 (1)
C21	−0.3063 (3)	0.2041 (3)	−0.2562 (3)	2.68 (8)
C22	−0.2422 (2)	0.1520 (2)	−0.1606 (3)	1.90 (7)
C23	−0.2630 (3)	0.1745 (3)	−0.0246 (3)	2.46 (8)
C24	−0.0575 (3)	−0.0459 (3)	−0.3710 (3)	2.29 (8)

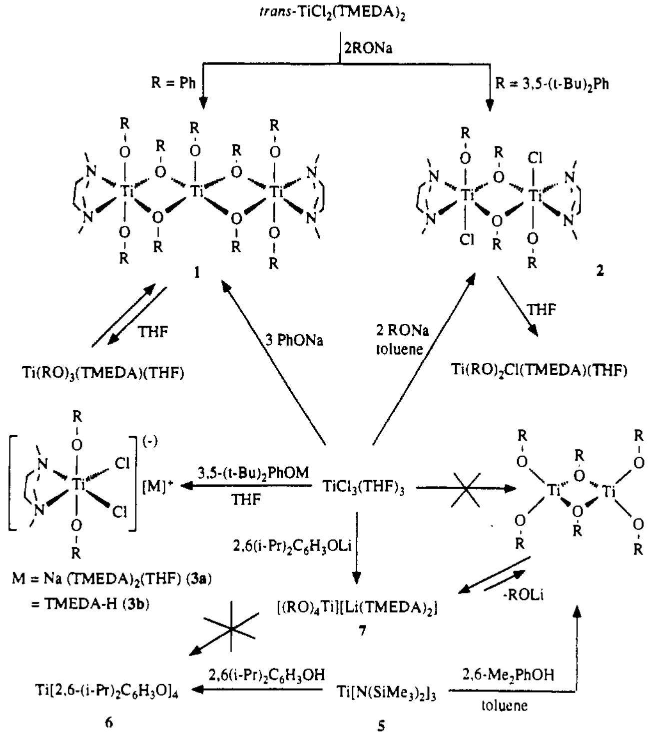
[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i a_j \mathbf{a}_i\cdot\mathbf{a}_j$.

Table V. Selected Bond Distances (Å) and Angles (deg)

Compound **1**			
Ti1–O1	2.067 (7)	Ti1–Ti2	3.264 (2)
Ti1–O2	2.030 (7)	Ti2–O3	1.902 (8)
Ti1–O5	1.802 (11)	Ti2–O1	2.089 (7)
Ti2–Ti1–Ti1a	151.92 (6)	N1–Ti2–N2	78.6 (2)
O1–Ti2–O2	72.8 (3)	O1–Ti1–O1a	154.8 (3)
O3–Ti2–O4	170.1 (4)	O2–Ti1–O2a	129.3 (3)
O3–Ti2–N1	88.7 (1)	O1–Ti1–O5	102.6 (2)
N1–Ti2–O2	104.6 (1)	O2–Ti1–O5	115.3 (2)
Compound **3b**			
Ti1–O1	1.899 (4)	Ti1–N1	2.288 (6)
Ti1–Cl1	2.492 (2)	Cl1⋯N3	3.080 (6)
O1–Ti1–O2	176.2 (2)	Cl1–Ti1–N1	172.6 (2)
N1–Ti1–N2	79.99 (2)	Cl1–Ti1–O1	90.3 (2)
Cl1–Ti1–Cl2	96.09 (8)		
Compound **4**			
Ti1–Ti1a	3.085 (2)	Ti1–O3	2.009 (2)
Ti1–O1	1.830 (2)		
O1–Ti1–O2	119.26 (9)	Ti1–O2–C1	154.6 (2)
O1–Ti1–O3	113.88 (9)	Ti1–O3–Ti1a	100.55 (8)
O2–Ti1–O3	108.32 (8)	O3–Ti1–O3a	79.45 (8)
Ti1–O1–C9	146.1 (2)	O3–Ti1–O3a	79.45 (8)

boiling toluene, treatment of **1** with pyridine caused formation of purple-red crystals of Ti(PhO)$_3$(TMEDA)(pyridine), which could not be transformed into the starting linear trimer. Complex **1** could also be prepared, although in much lower yield, from TiCl$_3$(THF)$_3$ and NaOPh in the presence of a light excess of TMEDA. Very air-sensitive light-pink crystals of the dimeric complex[17] [Ti(TMEDA)Cl]$_2$(μ-OR)$_2$ (**2**) were obtained from both Ti(II) and Ti(III) starting materials in the case of the substituted phenoxide [OPh(3,5-t-Bu)$_2$]$^-$. The dinuclear frame could be cleaved in THF even in this case, yielding very fine colorless needles of Ti(RO)$_2$Cl(TMEDA)(THF). Complex **2** could also be prepared from TiCl$_3$(THF)$_3$ and the appropriate amount of sodium phenoxide, only when the reaction was carried out in toluene. Conversely, the anionic, paramagnetic, and monomeric species [Ti(OR)$_2$Cl$_2$(TMEDA)][Na(THF)(TMEDA)$_2$] (**3a**) was isolated as bright-yellow air-sensitive crystals from reaction in THF. The similar anionic, monomeric, and paramagnetic complex [Ti(OR)$_2$Cl$_2$(TMEDA)][(TMEDA)H]$_{0.5}$ (**3b**) was obtained in good yield from the reaction of TiCl$_3$(THF)$_3$ with neat (3,5-t-Bu)$_2$PhOH in the presence of excess of TMEDA. In line with the marked dependence of the structure of these titanium(III) aryloxides on steric hindrance, the introduction of two methyl groups on the aromatic ring ortho positions, such as in 2,6-Me$_2$PhO–, led to formation of the homoleptic dinuclear complex [Ti(2,6-Me$_2$PhO)$_2$(μ-2,6-Me$_2$PhO)]$_2$ (**4**) as green-blue, very air-sensitive crystals. The complex could only be prepared, according to Scheme I, by reaction of Ti[N(SiMe$_3$)$_2$]$_3$ (**5**) with 3 equiv of ROH in toluene, since reaction of TiCl$_3$(THF)$_3$ and the corresponding sodium phenoxide in THF, followed by crystallization from toluene, gave different and ill-defined products. Finally, reaction of **5** with 3 equiv of the more bulky phenol 2,6-(i-Pr)$_2$C$_6$H$_3$OH exclusively gave the corresponding homoleptic and mononuclear[18] Ti(IV) derivative Ti[2,6(i-Pr)$_2$C$_6$H$_3$O]$_4$ (**6**). The result of the reaction was not modified when the reaction was carried out at low temperature or by slowly adding a dilute solution of phenol to a solution of **5**. Conversely, the reaction of the corresponding lithium salt 2,6-(i-Pr)$_2$C$_6$H$_3$OLi with TiCl$_3$(THF)$_3$ gave orange very air-sensitive crystals of the new paramagnetic and monomeric[19] Ti(III) species {Ti[2,6(i-Pr)$_2$C$_6$H$_3$O]$_4$}{Li(TMEDA)$_2$}·toluene (**7**). The intense blue-green color formed by the orange crystals of **7** in a solution of toluene suggests the existence of a reversible dissociation equilibrium of ROLi and formation of a dimeric species similar to **4**.

Scheme I



---

[17] The crystal structure of complex **2** was determined by X-ray diffraction analysis. Although, unfortunate poor scattering power prevented convergence to satisfactory values, the chemical connectivity was demonstrated. X-ray crystal structure: monoclinic, $P2_1/a$, a = 10.781 (7) Å, b = 25.053 (9) Å, c = 14.141 (1) Å, β = 104.08 (6)°, V = 3705 (4) Å^3, Z = 4, R = 0.118 (R_w = 0.082), for 228 parameters and 1035 significant reflections out of 4139. Ti–Ti = 3.296 (18) Å.

[18] X-ray crystal structure: monoclinic, $C2/c$, a = 24.88 (2) Å, b = 11.152 (6) Å, c = 20.82 (2) Å, β = 129.50 (5)°, V = 4458 (7) Å^3, Z = 4, R = 0.051 (R_w = 0.075), for 241 parameters and 2993 significant reflections out of 4149. (Minhas, R.; Gambarotta, S. Unpublished results.)

[19] X-ray crystal structure: orthorhombic, $Pbca$, a = 23.223 (7) Å, b = 25.198 (5) Å, c = 22.670 (3) Å, V = 13 265 (5) Å^3, Z = 8, R = 0.076 (R_w = 0.098), for 570 parameters and 4613 significant reflections out of 12 273. (Duchateau, R.; Gambarotta, S. Unpublished results.)

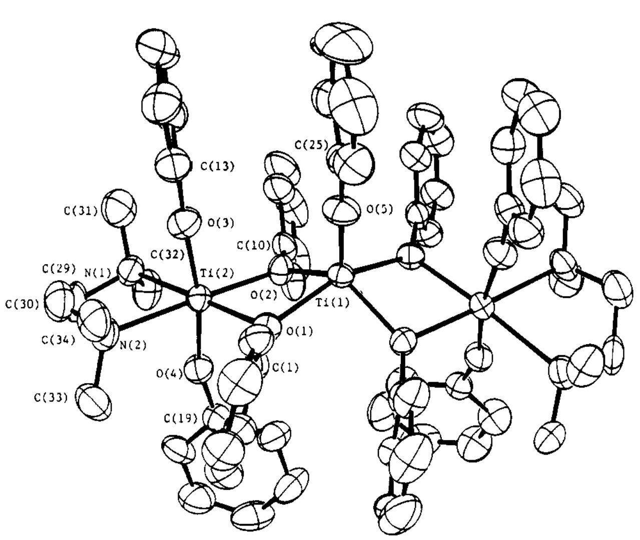


Figure 1. ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level.

Complexes **3a**, **3b**, and **7** have the magnetic moments expected for d^1 Ti(III) monomeric species. Conversely, complexes **2** and **4** showed remarkably lower values (μ_{eff} = 0.75 and 0.64 μ_B per Ti atom, respectively) which compare well with that observed for $[Ti(RO)_2Cl]_2$ (R = 2,6-Ph_2Ph) with a Ti_2Cl_2 core and significantly shorter Ti··Ti distance.[10] The magnetic moment of complex **1** (μ_{eff} = 1.69 μ_B per molecule), indicating less than one unpaired electron per trimetallic unit, is in line with those observed for **2** and **4**.

The structures of **1**, **2**,[17] **3b**, **4**, **6**,[18] and **7**[19] were determined by X-ray analysis. The linear trimeric structure of **1** [Ti2–Ti1–Ti2a = 151.92 (6)°] is composed of two terminal $Ti(PhO)_4$(TMEDA) octahedral fragments and one central square-pyramidal $Ti(PhO)_5$ fragment (Figure 1). The distorted coordination octahedron of the two terminal titanium atoms [O1–Ti2–O2 = 72.8 (3)°, O3–Ti2–O4 = 170.1 (4)°, O3–Ti2–N1 = 88.7 (1)°, N1–Ti2–O2 = 104.6 (1)°, N1–Ti2–N2 = 78.5 (2)°] is defined by two terminal and two bridging aryloxide oxygen atoms and by two nitrogens from one TMEDA molecule. The Ti–O bond distances formed by the two differently bonded alkoxides (terminal and bridging) are slightly different [Ti2–O3 = 1.902 (8) Å, Ti2–O1 = 2.089 (7) Å]. The central titanium atom is pentacoordinated, and its coordination geometry can be described as square-pyramidal (or distorted trigonal bipyramidal) [O1–Ti1–O1a = 154.8 (3)°, O2–Ti1–O2a = 129.3 (3)°, O1–Ti1–O5 = 102.6 (2)°, O2–Ti1–O5 = 115.3 (2)°]. Four bridging oxygens bound the basal plane while a fifth alkoxide occupies the apical site. The Ti–O distances formed by the bridging alkoxide groups [Ti1–O1 = 2.067 (7) Å, Ti1–O2 = 2.030 (7) Å] compare well with those of the terminal units. Conversely, the apical alkoxide forms a considerably shorter Ti–O distance [Ti1–O5 = 1.802 (11) Å], suggesting some extent of Ti–O multiple bonding. The Ti_2O_2 core is folded along the intermetallic vector [Ti1–O1–Ti2–O2 = 15.5 (1)°] and forms a Ti··Ti distance [Ti1–Ti2 = 3.264 (2) Å] which is not likely to be in agreement with the presence of a direct Ti–Ti bond.

Complex **3b** is mononuclear and composed of two different ionic moieties (Figure 2). The anion is formed by an octahedrally coordinated titanium atom with the coordination sphere defined by two aryloxide groups trans oriented [O1–Ti1–O2 = 176.2 (2)°], two nitrogen atoms of one TMEDA molecule [N1–Ti1–N2 = 79.99 (2)°], and two cis chlorines [Cl1–Ti1–Cl2 = 96.09 (8)°]. The Ti–O [Ti1–O1 = 1.899 (4) Å] and Ti–Cl [Ti1–Cl1 = 2.492 (2) Å] distances are normal. The cationic fragment consists of one-half molecule of TMEDA protonated at one of the two nitrogen atoms. Although the structure was not of sufficient quality to locate and refine the hydrogen atoms, the short contact observed between one TMEDA nitrogen atom and one chlorine atom of the anion suggests the presence of a Cl··H··N bridge.

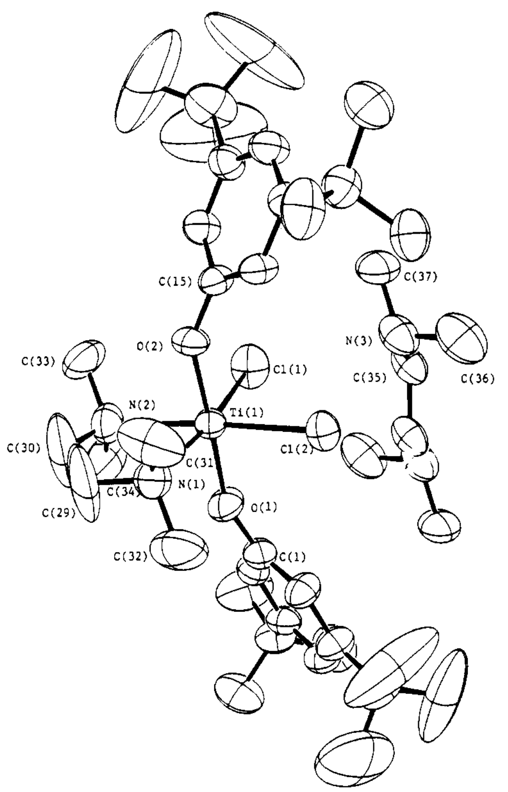


Figure 2. ORTEP plot of **3b**. Thermal ellipsoids are drawn at the 50% probability level.

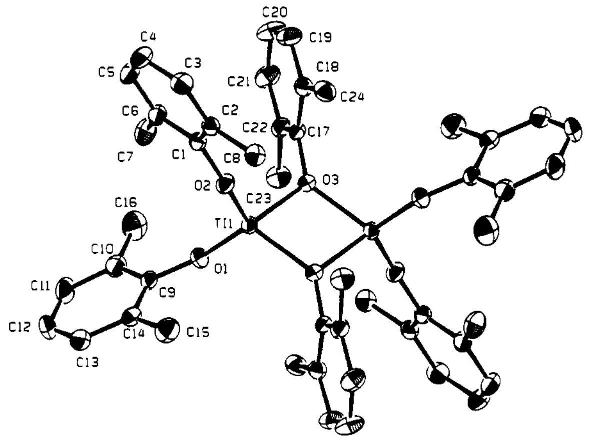
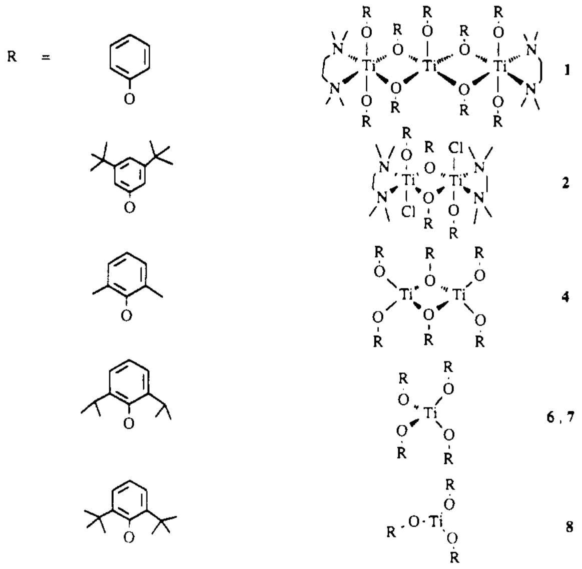


Figure 3. ORTEP plot of **4**. Thermal ellipsoids are drawn at the 50% probability level.

The homoleptic dinuclear complex **4** possesses a characteristic edge-sharing ditetrahedral geometry. The two identical and slightly distorted coordination tetrahedra centered on each titanium atom [O1–Ti1–O2 = 119.26 (9)°, O1–Ti1–O3 = 113.88 (9)°, O2–Ti1–O3 = 108.32 (8)°] are defined by two terminal and two bridging aryloxide oxygen atoms (Figure 3). The Ti–O distances formed by the two unequivalent oxygen atoms are different [Ti1–O1 = 1.830 (2) Å, Ti1–O3 = 2.009 (2) Å], suggesting some extent of Ti–O multiple bonding with the terminal aryloxide groups. Consistently, the angles subtended at the oxygen atoms [Ti1–O1–C9 = 146.1 (2)°, Ti1–O2–C1 = 154.6 (2)°] deviate significantly from the value expected for an sp^2 oxygen atom. The $Ti_2(OR)_2$ core is perfectly planar with the two bridging oxygen atoms in a trigonal planar coordination geometry [Ti1–O3–Ti1a = 100.55 (8)°, O3–Ti1–O3a = 79.45 (8)°]. The Ti··Ti distance [Ti1–Ti1a = 3.085 (2) Å] is in the expected range and compares well with those of complexes **1** and **2**.

Chart I



Discussion

The results listed in Chart I indicate that the steric hindrance of the aryloxide not only plays its usual and fundamental role in determining the geometry and the nuclearity of the Ti(III) derivatives but also possesses a rather unexpected capability of stabilizing the trivalent oxidation state. Unfortunately, it was not possible to obtain a consistent trend of reactions and products, due to the fact that different synthetic pathways have necessarily been used for the preparation of these complexes. However, it is possible to observe that the crystal structures of **1**, **2**, **4**, and **8** are indeed in line with the expected decrease of nuclearity and of metal coordination number along with the increase of the steric bulk of the aromatic ring. The very unusual trigonal planar geometry reported for complex **8**[12b] indicates that the increase of steric hindrance introduced by the two ortho *tert*-butyl groups prevents the aryloxide oxygen atoms from bridging, therefore hampering dimeric aggregation. Conversely, with the steric encumbrance slightly diminished, as in the case of 2,6-(i-Pr)$_2$C$_6$H$_3$O, homoleptic and monomeric species, either neutral and diamagnetic [(RO)$_4$Ti] (**6**) or anionic and paramagnetic [(RO)$_4$Ti]$^-$ (**7**), were obtained depending on the synthetic pathway employed. The anomalous formation of a Ti(IV) species indicates that the steric bulk of the phenoxide ligand is not sufficient in this case to stabilize the corresponding neutral titanium(III) aryloxide, either via dimerization or by providing a large organic matrix sufficient to protect the metal from further oxidation. The coordinatively unsaturated, neutral Ti(III) complex Ti[2,6-(i-Pr)$_2$C$_6$H$_3$O]$_3$, initially formed in the reaction of **5** with phenol, probably reacts very fast with the unreacted phenol to form the final Ti(IV) complex via evolution of H$_2$ (eq 1). While the

$$\mathrm{Ti(NR_2)_3} \xrightarrow{\mathrm{ROH}} [\mathrm{Ti(OR)_3}] \xrightarrow{\mathrm{ROH}} \mathrm{Ti(OR)_4} + \mathrm{H_2} \qquad (1)$$

explanation of the oxidation is in this case rather straightforward, it turns out to be more difficult to understand when complexes **1** and **2** are formed from the reaction of TiCl$_2$(TMEDA)$_2$ with the corresponding sodium phenoxides. These reactions also seem fairly clean and selective, since it was always possible to isolate the final products in reasonable yield. The oxidation of titanium(II) and titanium(III) aryloxides can be ascribed either to disproportionation or to the same type of oxidation observed during failed attempts to prepare vanadium(II) aryloxides using V(II) starting materials.[20] Although we did not find any evidence for the presence of coproducts in the reaction mixtures, the occurrence of oxidative deoxygenation pathways similar to those observed in the chemistry of chromium(II)[21] and yttrium aryloxides[22] cannot be excluded.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating grant) and the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Structural diagrams for **1** and **3b** and tables of structure refinement parameters, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **1**, **3b**, and **4** (39 pages). Ordering information is given on any current masthead page.

---

(20) (a) Gambarotta, S.; van Bolhuis, F.; Chiang, M. *Inorg. Chem.* **1987**, *26*, 4303. (b) Wilisch, W. C. A.; Scott, M. J.; Armstrong, W. H. *Inorg. Chem.* **1988**, *27*, 4333.

(21) Edema, J. J. H.; Gambarotta, S.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1991**, *30*, 1380.

(22) (a) Evans, W. J.; Sollberger, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 6095. (b) Poncelet, O.; Sartain, W. J.; Hubert-Pfalzgraf, H. L.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263. (c) Evans, W. J.; Sollberger, M. S.; Shreeve, J. L.; Olofson, J. M.; Hain, J. H.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 2492.