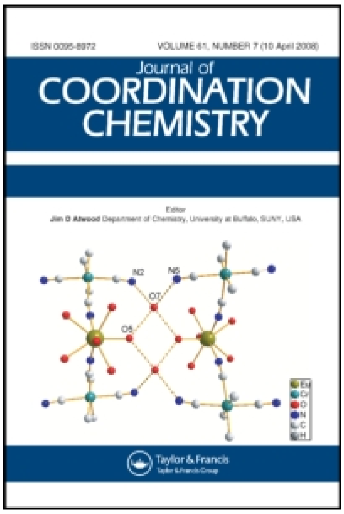

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SYNTHESIS, CHARACTERIZATION, AND REACTIONS OF MONOMERIC TITANIUM COMPLEXES CONTAINING A CHELATING BIS(PHENOLATE) LIGAND [1, 2]

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SYNTHESIS, CHARACTERIZATION, AND REACTIONS OF MONOMERIC TITANIUM COMPLEXES CONTAINING A CHELATING BIS(PHENOLATE) LIGAND [1, 2]

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The synthesis of Ti(iso)Cl_2 (iso = the dianion of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)) is described. Metathesis reactions of this complex with Grignard reagents, as well as alkali metal salts, yielded Ti(iso)X_2 (X = CH_3, CH_2Ph, CH_2SiMe_3, $OCMe_3$, or NMe_2). Reactions of the Ti-C bond in Ti(iso)$(CH_3)_2$ toward halogens, active hydrogen compounds, and acetone were studied. In addition, Ti(iso)(X)(Y) (X = Cl or CH_3; Y = OC_6H_2-2,6-$^tBu_2$-4-Me) could be prepared with the formation of only one coordination isomer. The new complexes have been thoroughly characterized by ^1H and ^{13}C NMR spectroscopies. The solid state structure of Ti(iso)Cl_2 was determined *via* single crystal X-ray diffraction methods. The complex is monomeric, with approximately tetrahedral geometry about the titanium ion. The structure of Ti(iso)Cl_2 is compared to that of Ti(ultra)Cl_2 (ultra = the dianion of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol)), which was redetermined to greater precision.

Keywords: titanium complexes, bidentate diphenolate ligands, eight-membered rings

For some time, we have been interested in utilization of the dianions of biphenols, such as 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (ultraH_2; commercially known as Ultranox 246), 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (isoH_2; commercially known as Isonox 129), 2,2′-thiobis(6-*tert*-butyl-4-methylphenol) (TBP), and related compounds, as potential bidentate ligands for the early transition metals [1-3]. These ligands, which form eight-membered chelate rings, hold the potential for controlling the nuclearity and electronic properties of the derived metal complexes through attenuation of the steric and electronic properties of the substituents on the phenyl rings and the bridge between the phenolic moieties. Complexes of Ti(IV) [1, 4-17] V(V) [3], V(III)

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[18], Zr(IV) [9, 10, 13], Mo(VI) [19], and W(VI) [19-22] containing either the diphenolato chelates listed above or related ligands have been reported previously, as well as the use of these complexes for olefin and diene polymerizations [4-9, 13, 14, 17, 21, 22]. A number of these complexes have been structurally characterized by single crystal X-ray diffraction methods [3, 10-12, 17-19].

In this contribution, we convey our results on the chemistry of a series of Ti complexes, Ti(iso)X_2 (iso = the dianion of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol); X = Cl, Br, I, CH_3, CH_2Ph, CH_2SiMe_3, $OCMe_3$, or NMe_2) and Ti(iso)(X)(Y) (X = Cl or CH_3; Y = OC_6H_2-2,6-$^tBu_2$-4-Me) [2]. Although Ti complexes of iso have been studied as *in situ* olefin polymerization catalysts [4], this is the first report of well-characterized, *monomeric*, early transition compounds with chelating, diphenolic ligands in which the bridge between the phenolic donors bears an alkyl substituent [23]. We also have determined the solid-state structure of Ti(iso)Cl_2 by X-ray diffraction methods, and compare it to the structure of Ti(ultra)Cl_2, which we have redetermined to further precision than previously reported [10].

EXPERIMENTAL SECTION

Materials and Methods

^1H and ^{13}C NMR spectra were recorded on either a Varian XL-300 or a Varian Gemini 300 spectrometer at 299.9 and 75.4 MHz, respectively. Chemical shifts for spectra obtained in C_6D_6 are reported in ppm relative to residual C_6H_6 at δ 7.16 (^1H) and δ 128.4 (^{13}C). Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, Georgia).

All manipulations were performed *via* standard Schlenk-type methods or in a nitrogen-filled Vacuum Atmospheres glovebox equipped with an efficient recirculating atmosphere purification system. Nitrogen and argon (Liquid Carbonic, prepurified) were purified further by passage through an oxygen and water removal column consisting of MnO supported on silica. Toluene, diethyl ether, *p*-dioxane, tetrahydrofuran (THF), heptane, and pentane were purified by standard methods and freshly distilled from sodium benzophenone ketyl under nitrogen. Acetone was distilled from anhydrous K_2CO_3 under nitrogen, while Me_3COH was distilled from sodium under argon.

Preparation of Ti(iso)Cl_2

The diphenol, isoH_2, (5.00 g, 11.4 mmol) was quickly added under nitrogen flush to a clean, dry Schlenk flask (100 mL), to which a condenser fitted with a three-way gas inlet adapter was attached. The entire apparatus was thrice evacuated and refilled with nitrogen. Toluene (80 mL) was syringed into the flask. The diphenol quickly dissolved and the flask was cooled to 0°C. $TiCl_4$ (2.16 g, 11.4 mmol) was added; the solution immediately turned dark orange. The reaction mixture was stirred at 0°C for 15 min, then refluxed overnight (at least 16 h). During this time, HCl evolution occurred.

The reflux condenser was replaced with a two-way gas inlet adapter. The solvent was removed under reduced pressure and the red-orange product was dried under vacuum overnight. The yield of Ti(iso)Cl_2 was essentially quantitative (6.21 g, 98%). *Anal.* Calcd. for $C_{30}H_{44}Cl_2O_2Ti$(%): C, 64.87; H, 7.98. Found: C, 65.03; H, 8.06. ^1H NMR (C_6D_6): δ 7.52 (d, 2 H, aryl), 7.23 (d, 2 H, aryl), 4.59 (q, 1 H, C*H*CH_3), 1.44 (d, 3 H, CHC*H*$_3$), 1.43 (s, 18 H, CMe_3), 1.23 (s, 18 H, CMe_3); ^{13}C NMR (C_6D_6): δ 164.2, 148.5, 142.1, 136.1, 122.4, 122.0, 36.1, 36.0, 35.4, 31.9, 30.7, 21.7.

Ti(ultra)Cl_2 was prepared as above for Ti(iso)Cl_2 with similar results. *Anal.* Calcd. for $C_{23}H_{30}Cl_2O_2Ti$(%): C, 60.41; H, 6.61. Found: C, 60.57; H, 6.46. ^1H NMR (C_6D_6): δ 6.84 (m, 4 H, aryl), 4.12 (d, 1 H, CH_2-bridge), 3.30 (d, 1 H, CH_2-bridge), 2.02 (s, 3 H, aryl-CH_3), 1.41 (s, 18 H, CMe_3).

Crystals of Ti(L)Cl_2 (L = iso or ultra) suitable for single crystal X-ray diffraction studies were obtained by slow vapor diffusion of heptane into a saturated solution of the titanium complex in diethyl ether under nitrogen.

Preparation of Ti(iso)(CH_3)$_2$

Ti(iso)Cl_2 (1.00 g, 1.80 mmol) was dissolved in diethyl ether (25 mL) under nitrogen in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The dark red-orange solution was cooled to −78°C and CH_3MgI (0.599 g, 3.60 mmol) in diethyl ether was added. The solution, which turned light yellow after a few minutes, was stirred at −78°C for 30 min, then at ambient temperature overnight.

p-Dioxane (0.317 g, 3.60 mmol) was added to the now green-yellow solution in order to aid in precipitation of magnesium salts. After stirring for 30 min, the gas inlet adapter was replaced with a "V-tube" connected to a two-sided filter frit containing 1.25 cm of Celite. After filtration into a Schlenk receiving flask, the solvent was removed from the golden yellow filtrate under reduced pressure. The pale yellow solid was dried under vacuum overnight to give Ti(iso)(CH_3)$_2$ (0.72 g, 78%). ^1H NMR (C_6D_6): δ 7.62 (d, 2 H, aryl), 7.34 (d, 2 H, aryl), 3.57 (q, 1 H, C*H*CH_3), 1.64 (s, 18 H, CMe_3), 1.50 (d, 3 H, CHC*H*$_3$), 1.47 (s, 3 H, Ti-CH_3), 1.38 (s, 3 H, Ti-CH_3), 1.31 (s, 18 H, CMe_3); ^{13}C NMR (C_6D_6): δ 159.2, 145.3, 137.9, 135.5, 122.1, 122.1, 61.2, 57.6, 36.1, 35.1, 35.0, 32.1, 30.8, 22.9.

Preparation of $Ti(iso)(CH_2Ph)_2$

$Ti(iso)Cl_2$ (1.00 g, 1.80 mmol) was dissolved in diethyl ether (25 mL) under nitrogen in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The dark red-orange solution was cooled to −78°C and $PhCH_2MgCl$ (0.543 g, 3.60 mmol) in diethyl ether was added. The solution, which turned light orange after a few minutes, was stirred at −78°C for 45 min, then at ambient temperature overnight.

p-Dioxane (0.317 g, 3.60 mmol) was added and the reaction mixture was treated exactly as above for $Ti(iso)(CH_3)_2$. The orange-yellow solid was dried under vacuum for 3 h to give $Ti(iso)(CH_2Ph)_2$ (0.70 g, 58%). ^1H NMR (C_6D_6): δ 7.62 (d, 2 H, phenolic aryl), 7.42 (d, 2 H, $CH_2C_6H_5$), 7.31 (d, 2 H, phenolic aryl), 7.25 (t, 2 H, $CH_2C_6H_5$), 7.05 (t, 1 H, $CH_2C_6H_5$), 6.90 (d, 4 H, $CH_2C_6H_5$), 6.66 (m, 1 H, $CH_2C_6H_5$), 3.62 (q, 1 H, $CHCH_3$), 3.15 (s, 2 H, Ti-CH_2), 2.84 (s, 2 H, Ti-CH_2), 1.62 (s, 18 H, CMe_3), 1.31 (d, 3 H, $CHCH_3$), 1.30 (s, 18 H, CMe_3); ^{13}C NMR (C_6D_6): δ 160.3, 147.5, 145.3, 141.9, 139.1, 135.4, 130.4, 130.0, 129.3, 127.3, 125.9, 123.8, 122.3, 121.9, 85.4, 84.2, 36.1, 35.1, 35.1, 32.1, 31.0, 23.4.

Preparation of $Ti(iso)(CH_2SiMe_3)_2$

$Ti(iso)Cl_2$ (1.00 g, 1.80 mmol) was dissolved in diethyl ether (25 mL) under nitrogen in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The dark red-orange solution was cooled to −78°C and Me_3SiCH_2MgCl (0.53 g, 3.6 mmol) in diethyl ether was added. The solution was stirred at −78°C for 30 min, then at ambient temperature for 2 h.

p-Dioxane (0.317 g, 3.60 mmol) was added and the reaction mixture was treated exactly as above for $Ti(iso)(CH_3)_2$. The pale yellow solid was dried under vacuum for 2 h to give $Ti(iso)(CH_2SiMe_3)_2$ (0.91 g, 76%). ^1H NMR (C_6D_6): δ 7.67 (d, 2 H, aryl), 7.35 (d, 2 H, aryl), 3.65 (q, 1 H, $CHCH_3$), 2.26 (s, 2 H, Ti-CH_2), 2.00 (s, 2 H, Ti-CH_2), 1.69 (d, 3 H, $CHCH_3$), 1.67 (s, 18 H, CMe_3), 1.31 (s, 18 H, CMe_3), 0.34 (s, 9 H, $SiMe_3$), 0.20 (s, 9 H, $SiMe_3$); ^{13}C NMR (C_6D_6): δ 159.7, 145.1, 138.5, 135.6, 122.3, 122.2, 85.8, 80.7, 36.2, 35.2, 32.1, 31.1, 23.7, 2.9, 2.4 (we believe that the resonance at 35.2 ppm is a superposition of two resonances).

Preparation of $Ti(iso)(OCMe_3)_2$

A mixture of $Ti(iso)Cl_2$ (1.00 g, 1.80 mmol) and $K(OCMe_3)$ (0.404 g, 3.60 mmol) was dissolved in diethyl ether (30 mL) under nitrogen in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The dark red-orange solution was cooled to −78°C and stirred for 1 h, then at ambient temperature for 2 h.

The solvent was removed from the now light-orange solution under reduced pressure. Heptane (20 mL) was added and the solids broken up. After thoroughly dissolving as much of the product complex as possible, the reaction mixture was filtered to give a pale yellow filtrate from which the solvent was removed under reduced pressure. The pale yellow solid was dried under vacuum for 5 h to give Ti(iso)$(OCMe_3)_2$ (0.78 g, 69%). ^1H NMR (C_6D_6): δ 7.64 (d, 2 H, aryl), 7.31 (d, 2 H, aryl), 5.02 (q, 1 H, C*H*CH_3), 1.79 (d, 3 H, CHCH_3), 1.55 (s, 18 H, CMe_3), 1.46 (s, 9 H, $OCMe_3$), 1.34 (s, 18 H, CMe_3), 1.31 (s, 9 H, $OCMe_3$); ^{13}C NMR (C_6D_6): δ 159.8, 143.7, 138.4, 136.1, 121.9, 121.7, 85.2, 84.5, 36.0, 35.1, 33.8, 32.9, 32.5, 32.2, 30.8, 22.4.

Preparation of Ti(iso)$(NMe_2)_2$

A mixture of Ti(iso)Cl_2 (1.00 g, 1.80 mmol) and $LiNMe_2$ (0.212 g, 4.16 mmol) was dissolved in tetrahydrofuran (30 mL) under nitrogen in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The dark red-orange solution was cooled to −78°C and stirred for 1 h, then at ambient temperature overnight.

The solvent was removed from the now light-orange solution under reduced pressure. Heptane (30 mL) was added and the solids broken up. After thoroughly dissolving as much of the product complex as possible, the reaction mixture was filtered to give a light orange filtrate from which the solvent was removed under reduced pressure. The orange-yellow solid was dried under vacuum for 5 h to give Ti(iso)$(NMe_2)_2$ (0.56 g, 54%). ^1H NMR (C_6D_6): δ 7.77 (d, 2 H, aryl), 7.44 (d, 2 H, aryl), 4.70 (q, 1 H, C*H*CH_3), 3.33 (s, 6 H, NMe_2), 2.76 (s, 6 H, NMe_2), 1.64 (d, 3 H, CHCH_3), 1.62 (s, 18 H, CMe_3), 1.40 (s, 18 H, CMe_3); ^{13}C NMR (C_6D_6): δ 158.7, 143.4, 136.6, 135.9, 122.5, 121.8, 45.1, 36.0, 35.2, 32.3, 32.2, 30.9, 24.2 (the resonances for the NMe_2 groups appear to be accidently equivalent).

Preparation of Ti(iso)(Cl)$(OC_6H_2$-2,6-$^tBu_2$-4-Me)

A mixture of Ti(iso)Cl_2 (0.50 g, 0.90 mmol) and 2,6-$^tBu_2$-4-MeC_6H_2OH (0.20 g, 0.90 mmol) was dissolved in toluene (20 mL) under nitrogen in a Schlenk flask (50 mL) fitted with a three-way gas inlet adapter. The dark red-orange solution was cooled to −78°C and stirred for 15 min, warmed to ambient temperature, then refluxed for five days under nitrogen. The solvent was removed; however, a ^1H NMR spectrum of the dried solid indicated that the reaction was only *ca.* 75% complete. The solid was redissolved in toluene (20 mL) and refluxed under nitrogen for an additional seven days. During the course of the two heating periods, HCl was evolved and the solution became lighter orange in color.

After cooling the reaction mixture, the solvent was removed under reduced pressure. The ^1H NMR of the dried residue indicated that the reaction was 92% complete. This crude product was slurried in pentane (5 mL) for 45 min, then filtered. The light orange-yellow solid on the filter was washed with pentane (2 × 2 mL) and dried under vacuum for 1.5 h to give Ti(iso)(Cl)(OC_6H_2-2,6-$^tBu_2$-4-Me) (0.33 g, 50%). ^1H NMR (C_6D_6): δ 7.51 (d, 2 H, aryl), 7.32 (d, 2 H, aryl), 7.06 (s, 2 H, aryl), 4.56 (q, 1 H, C*H*CH_3), 2.18 (s, 3 H, aryl-CH_3), 1.73 (d, 3 H, CHCH_3), 1.59 (s, 18 H, CMe_3), 1.58 (s, 18 H, CMe_3), 1.24 (s, 18 H, CMe_3); ^{13}C NMR (C_6D_6): δ 167.7, 160.2, 146.2, 141.1, 140.8, 136.4, 132.6, 126.2, 122.8, 121.3, 37.6, 36.1, 35.6, 35.2, 32.0, 31.4, 31.1, 21.9, 21.4.

Reactions of Ti(iso)$(CH_3)_2$

(a) With 2,6-$^tBu_2$-4-MeC_6H_2OH

A mixture of Ti(iso)$(CH_3)_2$ (0.50 g, 0.97 mmol) and 2,6-$^tBu_2$-4-MeC_6H_2OH (0.21 g, 0.97 mmol) was dissolved in toluene (20 mL) under nitrogen in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The solution was cooled to −78°C and stirred for 15 min, then warmed to ambient temperature and stirred overnight.

After the reaction mixture was filtered, the solvent was removed under reduced pressure. The ^1H NMR spectrum of the dried solid showed that it was a mixture of Ti(iso)(CH_3)(OC_6H_2-2,6-$^tBu_2$-4-Me) and free substituted phenol. The crude product was slurried in pentane (3 mL) for 30 min, then filtered. The orange-yellow solid on the filter was washed with pentane (1 mL, 2 mL, and finally with 5 mL) and dried under vacuum for 1 h to give a small amount (0.035 g) of Ti(iso)(CH_3)(OC_6H_2-2,6-$^tBu_2$-4-Me) that was ca. 92% pure by ^1H NMR spectroscopy. ^1H NMR (C_6D_6): δ 7.55 (d, 2 H, aryl), 7.36 (d, 2 H, aryl), 7.13 (s, 2 H, aryl), 3.70 (q, 1 H, C*H*CH_3), 2.23 (s, 3 H, aryl-CH_3), 1.65 (d, 3 H, CHCH_3), 1.61 (s, 18 H, CMe_3), 1.60 (s, 18 H, CMe_3), 1.28 (s, 18 H, CMe_3), 1.24 (s, 3 H, Ti-CH_3).

(b) With I_2

Under nitrogen, I_2 (0.493 g, 1.94 mmol) was added to a solution of Ti(iso)$(CH_3)_2$ (0.50 g, 0.97 mmol) in toluene (25 mL) in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The solution was stirred for 4 days at ambient temperature. Then, the solution was filtered and the solvent was removed under reduced pressure. The dark burgundy solid was slurried with heptane and filtered. The solid was washed several times with heptane and dried under vacuum overnight to give Ti(iso)I_2 (0.25 g, 35%). ^{1}H NMR (C_6D_6): δ 7.52 (d, 2 H, aryl), 7.23 (d, 2 H, aryl), 4.30 (q, 1 H, C*H*CH_3), 1.54 (s, 18 H, CMe_3), 1.41 (d, 3 H, CHC*H*$_3$), 1.24 (s, 18 H, CMe_3); ^{13}C NMR (C_6D_6): δ 165.5, 148.4, 143.1, 135.7, 122.4, 122.3, 37.8, 36.4, 35.4, 31.8, 31.1, 22.1.

(c) With Br_2

Under nitrogen, a solution of Br_2 (0.311 g, 1.94 mmol) in toluene (10 mL) in a pressure equalizing dropping funnel was slowly dripped into a cooled (−78°C) solution of Ti(iso)$(CH_3)_2$ (0.50 g, 0.97 mmol) in toluene (20 mL) over a period of 20 min. The solution was stirred for 1 h at −78°C after the addition was complete and overnight at ambient temperature. Then, the solution was filtered and the solvent was removed under reduced pressure. The brown orange solid was dried under vacuum overnight to give Ti(iso)Br_2 (0.43 g, 69%). *Anal.* Calcd. for $C_{30}H_{44}Br_2O_2Ti$(%): C, 55.92; H, 6.88. Found: C, 55.93; H, 7.04. ^{1}H NMR (C_6D_6): δ 7.51 (d, 2 H, aryl), 7.23 (d, 2 H, aryl), 4.51 (q, 1 H, C*H*CH_3), 1.47 (s, 18 H, CMe_3), 1.44 (d, 3 H, CHC*H*$_3$), 1.23 (s, 18 H, CMe_3); ^{13}C NMR (C_6D_6): δ 164.8, 148.5, 142.6, 136.0, 122.4, 122.1, 36.7, 36.2, 35.3, 31.8, 30.8, 21.8.

(d) With Me_3COH

Under nitrogen, Me_3COH (0.144 g, 1.94 mmol) was added to a cooled (−78°C) solution of Ti(iso)$(CH_3)_2$ (0.50 g, 0.97 mmol) in toluene (25 mL) in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The solution was stirred for 15 min at −78°C and overnight at ambient temperature. Then, the solvent was removed under reduced pressure and the tacky, pale yellow solid was slurried with pentane for 45 min. The pentane was removed under reduced pressure to give a yellow solid (0.56 g, 92%) that had a ^{1}H NMR spectrum that was identical to that of Ti(iso)$(OCMe_3)_2$ prepared from Ti(iso)Cl_2 and $KOCMe_3$ (*vide supra*).

(e) With acetone

Under nitrogen, acetone (0.126 g, 2.18 mmol) was added to a cooled (−78°C) solution of Ti(iso)$(CH_3)_2$ (0.50 g, 0.97 mmol) in toluene (25 mL) in a Schlenk flask (50 mL) fitted with a two-way gas inlet adapter. The solution was stirred for 30 min at −78°C and overnight at ambient temperature. Then, the solvent was removed under reduced pressure to give a yellow solid (0.46 g, 75%) that had a ^{1}H NMR spectrum that was identical to that of Ti(iso)$(OCMe_3)_2$ prepared from Ti(iso)Cl_2 and $KOCMe_3$ (*vide supra*).

X-ray Crystallography

Ti(iso)Cl_2, Mol. wt 555.5, monoclinic, space group $P2_1$ (no. 4), $Z = 2$, a = 11.164(5) Å, b = 9.812(4) Å, c = 15.185(8) Å, β = 108.88(4)°, V = 1573.9(13) $Å^3$, D_{calc} = 1.17 g cm^{-3}, $F(000)$ = 592, μ = 4.6 cm^{-1}.

A well-formed orange plate of Ti(iso)Cl_2 was covered with epoxy and mounted on the tip of a glass capillary. Axial photographs indicated the monoclinic crystal system. Unit cell parameters were determined from 25 well-centered, intense reflections in the range $15 \leq 2\Theta \leq 25°$.

A Siemens R3m diffractometer in the $\Theta/2\Theta$ mode with variable scan speed (2 to 20 deg min^{-1}) and graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) was used to measure 2214 unique reflections with $3 \leq 2\Theta \leq 45°$ (h, k, l = ±12, 10, 16) at ambient temperature. Of these, there were 1414 reflections with $|F_o| > 6|F_o|$. No decay was observed over the course of the data collection. Data were corrected for background, attenuators, Lorentz and polarization effects in the usual fashion, but not for absorption [24]. Heavy atoms were located *via* Patterson maps and full-matrix least-squares refinement was accomplished with the SHELXTL Plus package of programs. The Ti, Cl, O, and the C atoms of the methyl groups on the *t*-butyl substituents at the 4- and 4′-positions of the iso ligand were refined anisotropically. Hydrogen atom positions were calculated geometrically, fixed at a C-H distance of 0.96 Å, and not refined. The structure was refined to R = 0.061, R_w = 0.061 (data:parameter = 7.3) and R = 0.097 for all 2214 data.

Ti(ultra)Cl_2, Mol. wt 457.3, triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, a = 9.526(3) Å, b = 9.719(4) Å, c = 12.960(7) Å, α = 85.98(4)°, β = 87.66(4)°, γ = 86.15(3)°, V = 1193.5(1) $Å^3$, D_{calc} = 1.27 g cm^{-3}, $F(000)$ = 480, μ = 5.9 cm^{-1}.

A well-formed orange prism of Ti(ultra)Cl_2 was covered with epoxy and mounted on the tip of a glass capillary. Axial photographs indicated the triclinic crystal system. Determination of unit cell parameters, data collection and structure solution, and refinement methods were the same as above for Ti(iso)Cl_2, with the following changes.

A Siemens R3m diffractometer in the $\Theta/2\Theta$ mode with variable scan speed (3 to 20 deg min^{-1}) and graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) was used to measure 3011 unique reflections with $3 \leq 2\Theta \leq 45°$ (h, k, l = ±10, ±10, 13) at ambient temperature. Of these, there were 2262 reflections with $|F_o| > 6\,|F_o|$. No decay was observed over the course of the data collection. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically, fixed at a C-H distance of 0.96 Å, and not refined. The structure was refined to R = 0.045, R_w = 0.045 (data:parameter = 8.9) and R = 0.061 for all 3011 data.

In the original structure determination for this complex [10], only 1427 reflections with $|F_o| > 4|F_o|$ were used in the calculations. The utilization of a data set with more reflections having a higher intensity in the present case results in lower standard deviations for derived structural parameters.

RESULTS AND DISCUSSION

Synthesis and Reactivity of the New Titanium Complexes

The mildly water-sensitive complex, Ti(iso)Cl_2, was easily prepared in essentially quantitative yield by reaction of $TiCl_4$ with the diphenol in toluene at reflux under dry nitrogen. HCl evolution was observed in the effluent gas. We note that Ti(diphenolate)Cl_2 can also be prepared from the disodium salt of the diphenol and $TiCl_4$ [25], but the former synthesis is more direct and convenient.

Ti(iso)Cl_2 undergoes metathesis reactions with Grignard reagents to provide the organometallic complexes Ti(iso)R_2 (R = CH_3, CH_2Ph, or CH_2SiMe_3) in moderate to good yields. We could also effect substitution of the chloride ligands with alkoxide and amide salts, such as potassium *tert*-butoxide and lithium dimethylamide, to prepare Ti(iso)X_2 (X = $OCMe_3$ or NMe_2, respectively).

Curiously, aryl Grignard reagents appeared to cause significant reduction of the Ti center of Ti(iso)Cl_2, as evidenced by broad NMR spectra for the isolated solid products, even though Ti(ultra)$(C_6H_5)_2$ could be readily prepared using analogous reaction conditions [10, 12]. The reduction of $Ti(OC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)_2Cl_2$ by Me_3SiCH_2MgCl has been previously observed [26], while the reaction of homoleptic titanium alkyl complexes, TiR_4, with free, bulky monophenols is the preferred synthetic method for the preparation of $Ti(OAr)_2R_2$ [27, 28].

In order to probe the steric bulk of the iso ligand, we reacted Ti(iso)Cl_2 with 2,6-di-*tert*-butyl-4-methylphenol. Extended reflux (*ca.* 12 days) in toluene resulted in slow HCl evolution to give only *one* mono-substitution product, Ti(iso)(Cl)$(OC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)$. Without knowing whether the eight-membered ring is in a "boat" or "chair" conformation for this complex [12], it is not possible to determine with certainty which of the two inequivalent coordination sites is occupied by the monodentate ligands, though NMR evidence is suggestive (*vide infra*). We can say, however, that since this substitution was performed under conditions where equilibrium between the two coordination sites should have been attained, there appears to be a strong preference for one of the two sites by the monophenolate ligand.

Previously, Rothwell and coworkers found that $Ti(OC_6H_3\text{-}2,6\text{-}^tBu_2)_3Cl$ could be prepared only with difficulty [29]. The homoleptic aryloxides, $Ti(OC_6H_3\text{-}$

2,6-$R_2)_4$, are known for R = CH_3 and ^{i}Pr [30], but not for R = ^{t}Bu. On the other hand, Okuda, *et al.*, were able to prepare $Ti(ultra)_2$ [12], and simple adducts such as $Ti(ultra)Cl_2(THF)$ can be made [10, 12]. Thus, we conclude, tentatively, that one diphenolate ligand, such as iso and ultra, is smaller than two of the bulkier monophenolate ligands, such as OC_6H_3-2,6-$^tBu_2$. Further evidence can be derived from our successful preparation of $Ti(iso)(OCMe_3)_2$, while only the monoalkoxide complex, $Ti(OC_6H_3$-2,6-$^tBu_2$-4-$Me)_2(OCMe_3)Cl$ can be prepared [26]. However, the diphenolate ligand, iso, is apparently not small enough to accommodate two 2,6-di-*tert*-butylated monophenolates in the coordination sphere of the Ti ion.

The Ti-C bonds in $Ti(iso)(CH_3)_2$ undergo many reactions that are typical of such bonds [31]. For example, treatment of this dimethyl complex with molecular halogens (Br_2 or I_2) led to clean cleavage of both Ti-CH_3 bonds to give $Ti(iso)X_2$ (X = Br or I, respectively) and presumably CH_3X [32]. Protonolysis with *tert*-butyl alcohol gave $Ti(iso)(OCMe_3)_2$ and presumably methane. The latter dialkoxide complex could also be prepared by reaction of $Ti(iso)(CH_3)_2$ with acetone.

Protonolysis of $Ti(iso)(CH_3)_2$ with 2,6-di-*tert*-butyl-4-methylphenol led to isolation of $Ti(iso)(CH_3)(OC_6H_2$-2,6-$^tBu_2$-4-Me), which was slightly contaminated with free monophenol. As with $Ti(iso)(Cl)(OC_6H_2$-2,6-$^tBu_2$-4-Me), only one coordination isomer was isolated; we will discuss the NMR results below.

We attempted to thermolyze $Ti(iso)(CH_2Ph)_2$ under conditions similar to those used by Rothwell and coworkers with $Ti(OC_6H_2$-2,6-$^tBu_2)(CH_2Ph)_2$ that led to cyclometalation reactions involving a *tert*-butyl group of one of the phenolate ligands [27]. When $Ti(iso)(CH_2Ph)_2$ was refluxed for 12 h in toluene under nitrogen, the complex decomposed to unidentified products giving a very broad ^{1}H NMR resonance centered at *ca.* 1.3 ppm; no cyclometalation products could be detected. This is in keeping with the rigid nature of the diphenolic chelate and the inability of the *tert*-butyl groups to become involved in intramolecular C-H activation reactions.

NMR Studies

We found it difficult to obtain good microanalyses for most of the newly prepared titanium complexes. In general, carbon percentages were somewhat low, perhaps due to incomplete combustion and formation of metal carbides [28]. For the organometallic complexes, there was the added complication of trace magnesium salts that tenaciously held onto the complexes, even after precipitation with dioxane. In the end, we were successful in obtaining good microanalytical results for the initially prepared complexes, $Ti(iso)Cl_2$ and

Ti(iso)Br_2, which had been prepared from the organometallic complex, Ti(iso)$(CH_3)_2$.

We thoroughly characterized all of the new complexes *via* ^1H and ^{13}C NMR spectroscopies. In all cases, with the exception of Ti(iso)$(CH_3)(OC_6H_2$-2,6-$^tBu_2$-4-Me), which was contaminated with free monophenol, the number of resonances and their chemical shifts in the NMR spectra are consistent with the formulations of the new titanium compounds.

The spectra are relatively routine, but there are two significant points. For the complexes Ti(iso)X_2, two different sets of ^1H and ^{13}C NMR resonances are generally observed for X ligands that contain hydrogen and carbon. This indicates that the monodentate X ligands are inequivalent on the NMR time scale. We saw no broadened resonances that might result from "boat" to "chair" conformational equilibria, as seen for Ti(ultra)$(OCH_3)_2$ [12].

Second, the ^1H chemical shift of the methine resonance of the ethylidene bridge in Ti(iso)X_2 is very sensitive to the nature of the donor atom of the X ligand. This resonance, which appears as a quartet, ranges from 3.57 ($X = CH_3$) to 5.02 ppm ($X = OCMe_3$). The resonance for the axial hydrogen atom of the methylene bridge in Ti(ultra)X_2 behaves similarly [10, 12]. The more electronegative (or hard) that the donor atom of X is, the further downfield this resonance occurs.

Interestingly for Ti(iso)(Y)$(OC_6H_2$-2,6-$^tBu_2$-4-Me) (Y = Cl or CH_3) where only one coordination isomer is observed, the methine resonance for Y = Cl is almost identical to that for Ti(iso)Cl_2 (4.56 *vs.* 4.59 ppm). Similarly for Y = CH_3, we find a methine chemical shift of 3.70 ppm *vs.* 3.57 ppm for Ti(iso) $(CH_3)_2$. These results are somewhat unexpected given the sensitivity of this resonance to the nature of the donor atoms of the monodentate ligands. If we speculate that the chloro and methyl ligands of the "mixed ligand" complexes occupy the same coordination site (axial or equatorial), then it appears that the methine chemical shift is influenced more by the donor atom at one of these two coordination positions. In the preferred boat conformation for the eight-membered ring of these complexes, the axial coordination site on the titanium ion is probably more sterically congested than the equatorial one and is spatially close to the axial methine hydrogen atom [12]. The present results then suggest that the small chloro or methyl ligand in the "mixed ligand" complexes occupies the axial coordination site, thus affecting the chemical shift of the methine group.

X-ray Diffraction Studies

Single crystal X-ray analysis of Ti(iso)Cl_2 (Figure 1) revealed that the structure is essentially analogous to that of Ti(ultra)Cl_2 (Figure 2). The asymmetric unit in each crystal consists of one discrete, monomeric complex, with tetrahedral coordination about the titanium ion. Apparently, the *tert*-butyl groups at the 6- and 6′-positions of the chelating diphenolate ligand prevent dimerization, although there is enough room to form five-coordinate adducts, such as Ti(ultra)Cl_2(THF) [12]. This contrasts with $Ti(OC_6H_5)_2Cl_2$, which is dimeric in the solid state [33], as well as in solution [34]. This dimer readily forms adducts of the type $Ti(OC_6H_5)_2Cl_2L_2$ [33], while monomeric $Ti(OC_6H_3\text{-}2,6\text{-}Ph_2)_2Cl_2$ [35] and $Ti(OC_6H_3\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}Me)_2Cl_2$ [26] reportedly do not form adducts.

Both Ti(iso)Cl_2 and Ti(ultra)Cl_2 contain a flattened boat conformation for the eight-membered ring, which has been observed in analogous transition metal complexes containing the ultra ligand [3, 10-12, 18, 19] however, there are subtle differences between the two complexes. The boat conformation in Ti(iso)Cl_2 (Figure 3) is more closed than that in Ti(ultra)Cl_2 (Figure 4). This is illustrated by the closing of the dihedral angle between the planes defined by [Ti(1), O(1), O(2)] and [C(6), C(7), C(8)] from 71° in Ti(ultra)Cl_2 to 60° in Ti(iso)Cl_2. The

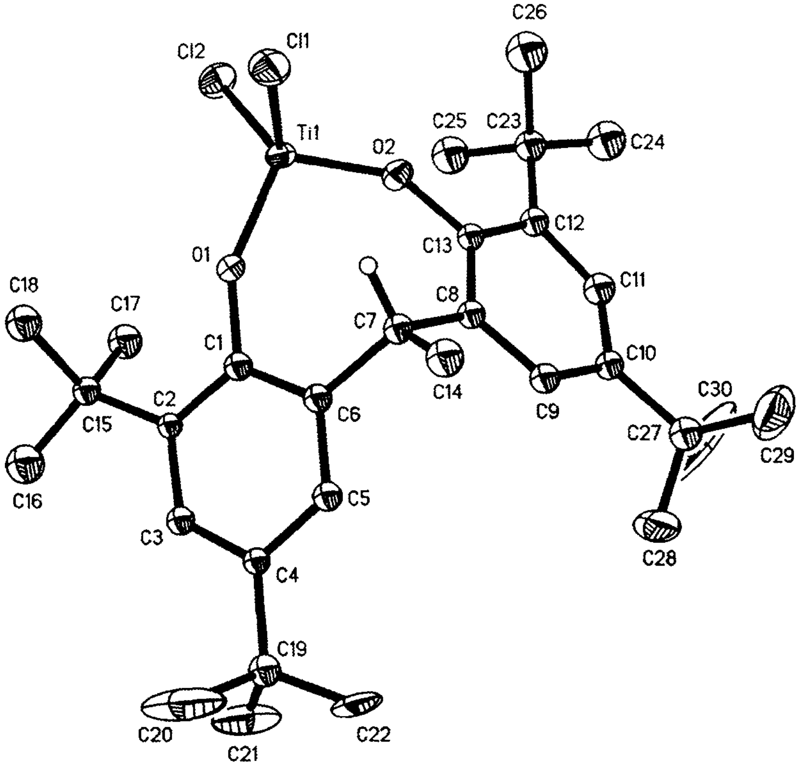

FIGURE 1 Molecular structure and atom numbering scheme for Ti(iso)Cl_2.

one-carbon bridge between the phenolate moieties is bent slightly further away from the phenyl rings and closer to the titanium ion in Ti(iso)Cl_2, possibly due to unfavorable steric interactions between the C(14) methyl group and ring hydrogen atoms on C(5) and C(9). The axial hydrogen atom on the bridging carbon atom C(7) is only 2.538 Å from the metal ion in Ti(iso)Cl_2, but is 2.723 Å distant in Ti(ultra)Cl_2.

Bond lengths and angles within the coordination sphere (Table I) and ligands for both complexes are as expected for similar aryloxo titanium complexes [36]. For example, the Ti-Cl and Ti-O bond lengths in Ti(iso)Cl_2 and Ti(ultra)Cl_2 are comparable to those found for $[Ti(OC_6H_5)_2Cl_2]_2$ [33] and $Ti(OC_6H_3\text{-}2,6\text{-}Ph_2)_2Cl_2$ [35]. However, the bonds in the coordination sphere of Ti(iso)Cl_2 and Ti(ultra)Cl_2 are somewhat shorter than those found in five-coordinate Ti(ultra)Cl_2(THF) [12] and six-coordinate $Ti(OC_6H_3\text{-}2,6\text{-}Ph_2)_2Cl_2(THF)_2$ [37]. The longer metal-to-ligand bond lengths in the latter complexes may result from stronger steric repulsions due to the higher coordination numbers. The Ti-O bond

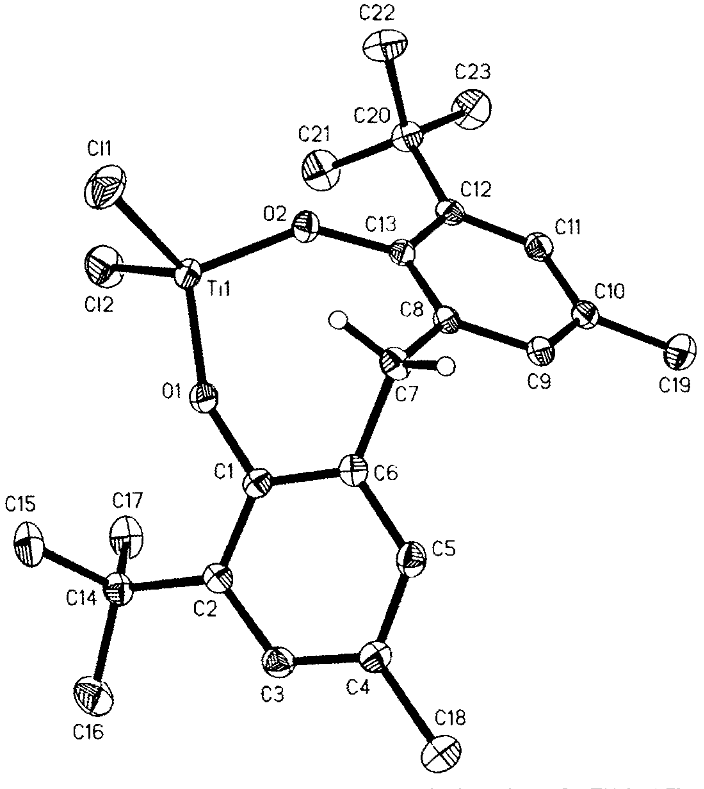

FIGURE 2 Molecular structure and atom numbering scheme for Ti(ultra)Cl_2.

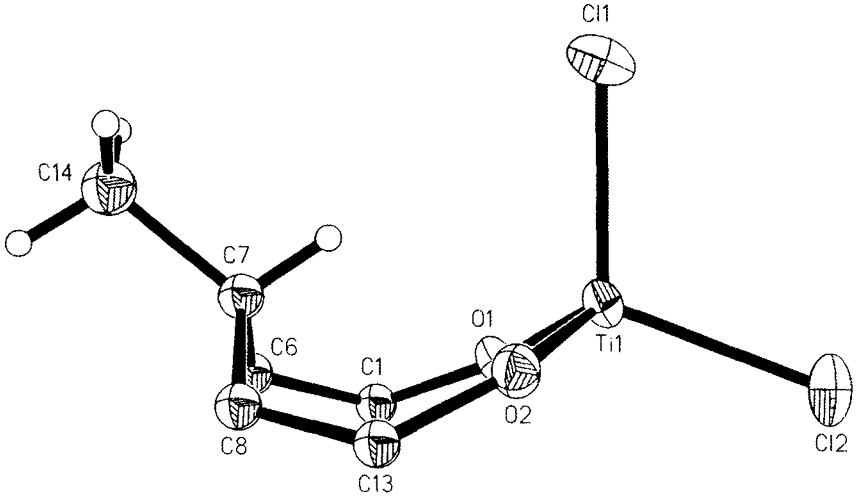

FIGURE 3 View of the conformation of the eight-membered ring of Ti(iso)Cl_2. Ti(1), Cl(1), and Cl(2) are in the plane of the paper.

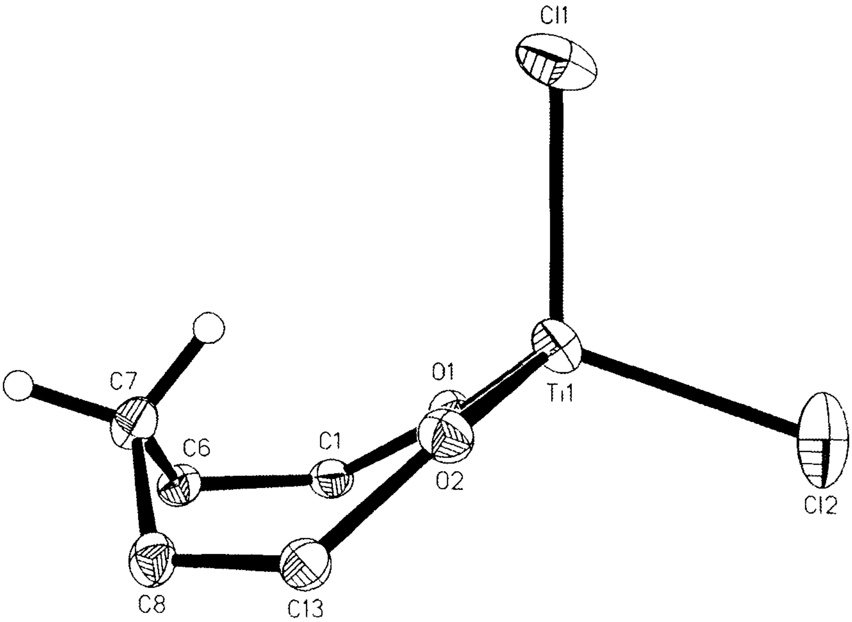

FIGURE 4 View of the conformation of the eight-membered ring of Ti(ultra)Cl_2. Ti(1), Cl(1), and Cl(2) are in the plane of the paper.

TABLE I Selected bond lengths (Å) and angles (°) for Ti(iso)Cl_2 and Ti(ultra)Cl_2

	Ti(iso)Cl_2	Ti(ultra)Cl_2
Ti(1)-O(1)	1.752(6)	1.746(3)
Ti(1)-O(2)	1.735(10)	1.766(3)
Ti(1)-Cl(1)	2.228(5)	2.224(2)
Ti(1)-Cl(2)	2.215(5)	2.207(2)
Cl(1)-Ti(1)-Cl(2)	110.9(2)	109.5(1)
Cl(1)-Ti(1)-O(1)	110.0(4)	110.8(1)
Cl(2)-Ti(1)-O(1)	111.5(3)	108.4(1)
Cl(1)-Ti(1)-O(2)	107.7(3)	110.8(1)
Cl(2)-Ti(1)-O(2)	110.6(3)	110.6(1)
O(1)-Ti(1)-O(2)	105.9(4)	106.5(1)
Ti(1)-O(1)-C(1)	151.3(8)	155.8(3)
Ti(1)-O(2)-C(13)	148.3(6)	143.1(3)

lengths for Ti(iso)Cl_2 and Ti(ultra)Cl_2 are also shorter than those found for Ti(ultra)$(CH_3)_2$ [10], $Ti(OC_6H_3\text{-}2,4,6\text{-}{}^tBu_3)_2(NMe_2)_2$ [38], and $Ti(OC_6H_3\text{-}2,6\text{-}{}^tBu_2)_2(NMe_2)_2$ [39], where stronger σ- and/or π-donor ligands are present.

The Ti-O-C angles in titanium aryloxo complexes are often nearly linear. In $[Ti(OC_6H_5)_2Cl_2]_2$ [33] and $Ti(OC_6H_3\text{-}2,6\text{-}Ph_2)_2Cl_2$ [35], this angle is 165.9(6)° and 168.5°, respectively, while for $Ti(OC_6H_3\text{-}2,6\text{-}{}^tBu_2)_2(NMe_2)_2$ [39], Ti-O-C angles of 177.1(2)° and 174.6(2)° are observed. The chelating nature of the diphenolate ligands in this study prevent the Ti-O-C angles from approaching linearity. Even so, the Ti-O bond lengths for Ti(iso)Cl_2 and Ti(ultra)Cl_2 are quite short, once again demonstrating the tenuous relationship between metal-oxygen bond lengths and the metal-oxygen-carbon bond angles in aryloxo metal complexes [36].

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