

Monopentamethylcyclopentadienyltitanium(IV) halo-alkoxides, alkyl-alkoxides and acetylacetonates

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Abstract

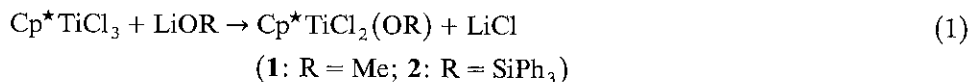
Reactions of $(C_5Me_5)TiCl_3$ with lithium alkoxides in 1:1 or 1:2 molar ratio have given the halo-alkoxides $(C_5Me_5)TiCl_{3-n}(OR)_n$ ($n=1$, $R=Me, SiPh_3$; $n=2$, $R=SiPh_3$) and $(C_5Me_5)TiCl(O_2R')$ ($R'=C_6H_4, C_6H_3-4^tBu$). Protonolysis of $(C_5Me_5)TiMe_3$ with $HOSiPh_3$ and Hacac gives $(C_5Me_5)TiMe(OSiPh_3)_2$ and $(C_5Me_5)TiMe_2(acac)$, and $(C_5Me_5)TiCl_2Me$ likewise gives $(C_5Me_5)TiCl_2(OC_6H_3-2,6-Me_2)$ and $(C_5Me_5)TiCl_2(acac)$. The crystal structure of $(C_5Me_5)TiCl_2(OC_6H_3-2,6-Me_2)$ has been determined and shows it to be monomeric, with a symmetry plane, a Ti–O distance of 1.785(2) Å, and a Ti–O–C angle of 162.3(2)°.

Introduction

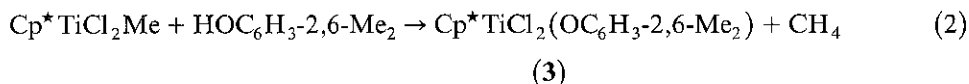
We are engaged in a study of the chemistry of monopentamethylcyclopentadienyltitanium(IV) derivatives, and have previously reported a series of alkyls, oxides, and carboxylates [1]. These compounds are formally 12-electron species, and the presence of strong π -donor ligands in the coordination sphere of the metal could help to reduce its electronic deficiency, which otherwise often leads to an uncontrollable reactivity. The alkoxide group is ideally suited for this purpose, and in this paper we describe several monopentamethylcyclopentadienyl titanium(IV) halo- and alkyl-alkoxides and related acetylacetonates, and present the results of determination of the crystal structure of $(C_5Me_5)TiCl_2(OC_6H_3-2,6-Me_2)$. Several monocyclopentadienyl titanium alkoxides and halo-alkoxides have been described previously [2], but only a few structural X-ray determinations have been reported [3].

Results and discussion

Pentamethylcyclopentadienyltitanium dihalo monoalkoxides can be readily prepared by anion exchange reactions involving the corresponding lithium alkoxides ($Cp^* = C_5Me_5$):

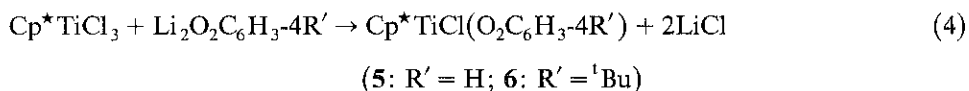
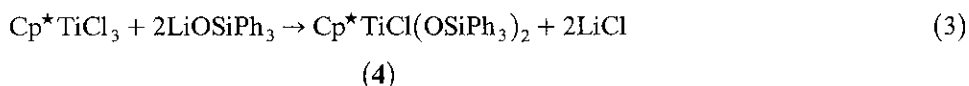


Dichloromonoalkoxides can alternatively be prepared by alcoholysis of the Ti–C bond of Cp*TiCl₂Me:

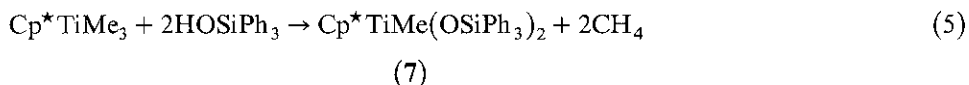


¹H-NMR spectra of compounds **1–3** in CDCl₃ show only one Cp* resonance along with the corresponding signals for R. **3** is monomeric in the solid state, as shown by X-ray crystallography, **2** is probably also monomeric, but **1**, incorporating the smaller methoxide substituent is associated, being dimeric in the gas as indicated by mass spectrometry data.

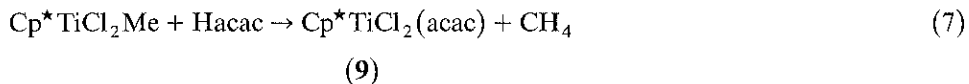
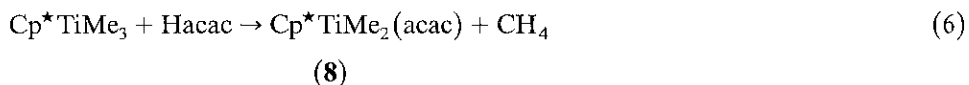
Monochloro-dialkoxo derivatives which contain two monodentate or one bidentate alkoxy groups can be similarly prepared, according to eq. 3 and 4, although in the case of the methoxide a mixture of the mono-, di- and tri- substituted derivatives is obtained:



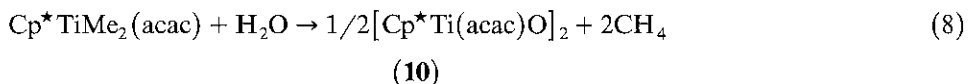
Pentamethylcyclopentadienyl methyl alkoxides can be obtained by alcoholysis of Cp*TiMe₃; in the case of the bulky triphenylsiloxide group only two siloxo groups can be introduced even when an excess of the alcohol is used



The dimethyl acetylacetonato derivative **8** is also readily obtained by the same route (eq. 6) and the dichloro acetylacetonate **9** can be obtained by the method used for **3** but, starting from Cp*TiCl₂Me (eq. 7):



The remaining titanium–methyl bond of **7** is less reactive, probably due to the presence of the two bulky triphenylsiloxide substituents, but the Ti–C bonds of **8** are easily hydrolyzed:



According to molecular weight measurements compounds **8** and **9** are monomeric in solution, but **10** is dimeric, and the appearance of a strong broad band at 767 cm⁻¹ in the IR spectrum suggests the presence of Ti–O–Ti bonds. All the new compounds were characterized by ¹H-NMR spectroscopy, and relevant data are presented in Table 1.

Table 1

¹H-NMR data for the new compounds ^a

| Compound | $\delta(\text{Cp}^*)$ | $\delta(\text{OR})$ | $\delta(\text{Me-Ti})$ |
|---|-----------------------|----------------------------------|------------------------|
| $\text{Cp}^*\text{TiCl}_2(\text{OMe})$ (1) | 2.10 | 4.18 (s, 3H) | |
| $\text{Cp}^*\text{TiCl}_2(\text{OSiPh}_3)$ (2) | 2.12 | 7.40 (m) 7.65 (m) | |
| $\text{Cp}^*\text{TiCl}_2(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)$ (3) | 2.22 | 2.28 (s, 6H) 6.90 (m) | |
| $\text{Cp}^*\text{TiCl}(\text{OSiPh}_3)_2$ (4) | 1.81 | 7.20 (m) 7.60 (m) | |
| $\text{Cp}^*\text{TiCl}(\text{O}_2\text{C}_6\text{H}_4)$ (5) | 2.09 | 6.81 (m) 6.89 (m) 7.24 (m) | |
| $\text{Cp}^*\text{TiCl}(\text{O}_2\text{C}_6\text{H}_3\text{-4-}^i\text{Bu})$ (6) | 2.09 | 6.92 (m) 6.76 (m) 1.30 (s) | |
| $\text{Cp}^*\text{TiMe}(\text{OSiPh}_3)_2$ (7) | 1.70 | 7.24 (m) 7.60 (m) | 0.77 (s, 3H) |
| $\text{Cp}^*\text{TiMe}_2(\text{acac})$ (8) | 1.79 | 2.12 (s, 6H) 5.85 (s, 1H) | 0.29 (s, 6H) |
| $\text{Cp}^*\text{TiCl}_2(\text{acac})$ (9) | 2.06 | 1.97 (s, 6H) 5.10 (s, 1H) | |
| $[\text{Cp}^*\text{Ti}(\text{acac})\text{O}]_2$ (10) | 1.79 | 2.01 (s, 6H) 5.50 (s, 1H) | |

^a In CDCl_3 excepting those of **9** and **10** in C_6D_6 .*X-Ray structure of $\text{Cp}^*\text{TiCl}_2(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)$ (3)*

The molecular structure of **3** is shown in Fig. 1, the final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are presented in Table 2, and selected bond distances and angles in Table 3. The compound is

Table 2

Positional parameters for compound **3** and their esd's between parentheses

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> (Å ²) ^a |
|-------|------------|------------|------------|---|
| Ti(1) | 0.71935(3) | 0.250 | 0.67095(6) | 2.669(7) |
| Cl(1) | 0.80536(3) | 0.12775(4) | 0.62912(8) | 4.65(1) |
| O(1) | 0.6586(1) | 0.250 | 0.4837(2) | 3.27(4) |
| C(1) | 0.5953(2) | 0.250 | 0.8249(4) | 3.91(6) |
| C(2) | 0.6415(1) | 0.3281(1) | 0.8740(3) | 3.80(4) |
| C(3) | 0.7149(1) | 0.2983(1) | 0.9570(3) | 3.66(4) |
| C(4) | 0.5924(2) | 0.250 | 0.3753(3) | 3.09(5) |
| C(5) | 0.5593(1) | 0.3337(1) | 0.3221(3) | 3.67(4) |
| C(6) | 0.4891(1) | 0.3315(2) | 0.2201(3) | 4.58(5) |
| C(7) | 0.4536(2) | 0.250 | 0.1717(4) | 5.02(8) |
| C(11) | 0.5103(2) | 0.250 | 0.7458(5) | 6.4(1) |
| C(21) | 0.6151(2) | 0.4266(2) | 0.8566(3) | 6.20(6) |
| C(31) | 0.7787(2) | 0.3574(2) | 1.0425(3) | 5.87(6) |
| C(51) | 0.5983(2) | 0.4228(2) | 0.3736(3) | 5.29(6) |

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \times [a^2 \times B_{1,1} + b^2 \times B_{2,2} + c^2 \times B_{3,3} + ab(\cos \gamma) \times B_{1,2} + ac(\cos \beta) \times B_{1,3} + bc(\cos \alpha) \times B_{2,3}]$.

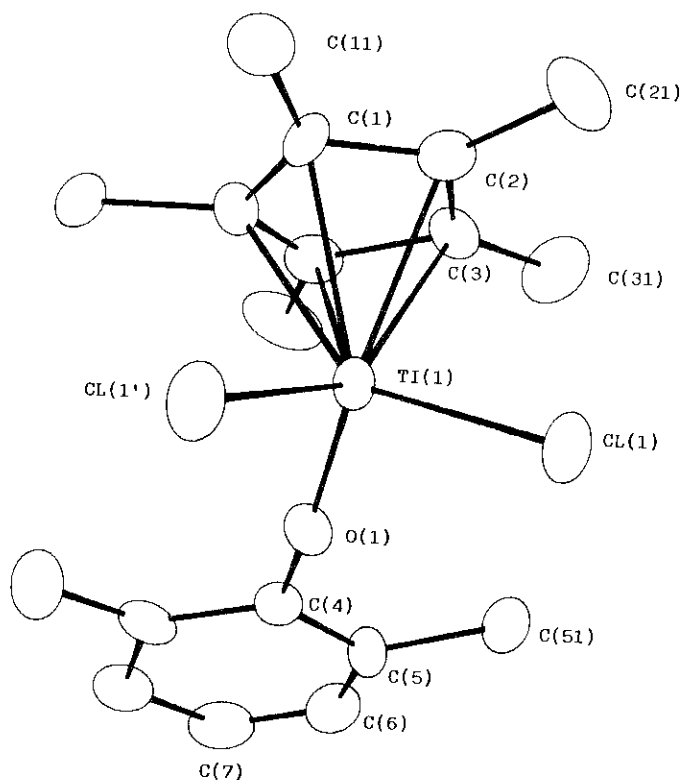


Fig. 1. Structure of compound **3** with the numbering scheme employed

monomeric, and has a classical three-legged piano stool structure with a symmetry plane defined by Ti–O–Cp* (centroid). The Cp(centroid)–Ti–substituent angles vary from 113.8 for Cl1 to 120.3° for O1; the angles formed by the legs are between 101.1(2) and 103.3(1°). The Cl1, Cl1', O1 plane is nearly parallel to the Cp* best plane [dihedral angle 3(1)°] and the phenyl ring of the aryloxy ligand is also almost parallel to them [dihedral angles: 7.0(5)° with Cp* and 9.8(3)° with the Cl1, Cl1', O1 plane]. This arrangement of the C₆H₃-2,6-Me₂ ring is very favourable in terms of steric effects, and associated with a large Ti–O–C angle [162.3(2)°]; this wide angle and the short Ti–O distance of 1.785(2) Å indicate significant multiple character for the Ti–O bond due to O → Ti π-electron donation [3,4]. The distances

Table 3

Selected bond distances (Å) and angles (°) for compound **3**

| | | | |
|-----------------------|-----------|----------------|----------|
| Ti(1)–Cl(1) | 2.2736(6) | Ti(1)–O(1) | 1.785(2) |
| Ti(1)–C(1) | 2.329(3) | O(1)–C(4) | 1.366(3) |
| Ti(1)–C(2) | 2.341(2) | Ti(1)–C(3) | 2.398(2) |
| Ti(1)–Cp ^a | 2.034 | | |
| Cl(1)–Ti(1)–Cl(1') | 103.3(2) | Cp–Ti(1)–O(1) | 120.3 |
| Cl(1)–Ti(1)–O(1) | 101.7(1) | Cp–Ti(1)–Cl(1) | 113.8 |
| Ti(1)–O(1)–C(4) | 162.3(2) | | |

^a Cp is the centroid of the C₅Me₅ ring.

from titanium to the chlorine and cyclopentadienyl ring carbons are in the normal range.

Experimental

All reactions were carried out under N_2 by Schlenk techniques. Hexane was refluxed over Na/K amalgam and distilled under N_2 , diethyl ether and tetrahydrofuran over Na/benzophenone, and CH_2Cl_2 over P_2O_5 . The lithium alkoxides were prepared from the corresponding alcohols (freshly distilled or sublimed) and *n*-butyl lithium in ether or THF. Cp^*TiCl_3 [5] and Cp^*TiMe_3 [6] were prepared by published procedures. IR spectra were recorded on Perkin–Elmer 599 and 883 spectrometers and 1H -NMR spectra on a Varian FT-80A spectrometer. Electron impact mass spectra were obtained at 70 eV with a Hewlett–Packard 5988 spectrometer. C and H analysis was carried out with a Perkin–Elmer 240B micro-analyzer, and molecular weight measurements were determined with a Knauer vapour pressure osmometer.

$(C_5Me_5)TiCl_2(OMe)$ (1)

A suspension of 0.25 g (0.86 mmol) of Cp^*TiCl_3 and 0.033 g (0.86 mmol) LiOMe was stirred in 50 ml of hexane for 3 h, then filtered, and the yellow solution concentrated to half its volume and allowed to cool overnight. The yellow crystals of **1** were filtered, washed with hexane and dried. Yield 82%. Analysis: found: C, 46.95; H, 6.57. $C_{11}H_{18}Cl_2OTi$ calcd.: C, 46.34; H, 6.36%. MS: *m/e* [assignment, rel. int. (%)] 568 [M^+ , 1.8], 533 [$(M - Cl)^+$, 1], 518 [$(M - Cl - Me)^+$, 1], 483 [$(M - 2Cl - Me)^+$, 3.6], 383 [$(M - Cp^* - 2Cl - Me)^+$, 22].

$(C_5Me_5)TiCl_2(OSiPh_3)$ (2)

A solution of 0.287 g (1.016 mmol) of $LiOSiPh_3$ in 20 ml of THF was added dropwise to a stirred solution of 0.3 g (1.037 mmol) of Cp^*TiCl_3 in 30 ml THF. Stirring was continued for 3 h and the solution then filtered and evaporated to dryness. The resulting orange oil was extracted with several portions of hexane, and the combined extracts filtered and concentrated and kept at ca $-30^\circ C$ overnight. The yield of orange **2** was 89%. Analysis: found, C, 63.75; H, 5.28. $C_{28}H_{30}Cl_2OSiTi$ calcd.: C, 63.52; H, 5.71%. MS *m/e* [assignment, rel. int. (%)] 528 [M^+ , 1], 492 [$(M - Cl - H)^+$, 2], 451 [$(M - Ph)^+$, 5], 374 [$(M - 2Ph)^+$, 3], 276 [Ph_3SiOH , 14], 199 [Ph_2SiOH , 57].

$(C_5Me_5)TiCl_2(OC_6H_3-2,6-Me_2)$ (3)

2,6-Dimethylphenol (0.154 g, 1.26 mmol) was added to a solution of 0.34 g (1.26 mmol) of Cp^*TiCl_2Me in 30 ml of dichloromethane. The mixture was stirred overnight then concentrated to half volume and kept at $-30^\circ C$ for 24 h. Red crystals of **3** were isolated in 85% yield. Analysis: found, C, 56.9; H, 6.4. $C_{18}H_{24}Cl_2OTi$: calcd.: 57.6% C, 6.5% H; found, C, 57.6; H, 6.5%. MS *m/e* [assignment, rel. int. (%)] 374 [M^+ , 64], 339 [$(M - Cl)^+$, 15], 304 [$(M - 2Cl)^+$, 4], 253 [$(M - OC_6H_9)^+$, 74].

$(C_5Me_5)TiCl(OSiPh_3)_2$ (4)

A solution of 0.88 g (3.11 mmol) of $LiOSiPh_3$ in 20 ml of THF was added dropwise to 0.3 g (1.037 mmol) of Cp^*TiCl_3 in 30 ml of THF and the solution was

refluxed overnight then allowed to cool. The solvent was removed under vacuum and the residual yellow oil was dissolved in hexane. The solution was filtered, concentrated to small volume and cooled to -78°C . Yellow **4** crystallized in 90% yield. Analysis: found: C, 71.3; H, 5.6. $\text{C}_{46}\text{H}_{45}\text{ClO}_2\text{Si}_2\text{Ti}$ calcd., 71.8% C, 5.9% H; calcd.: C, 71.8; H, 5.9%. MS *m/e* [assignment, rel. int. (%)] 768 [M^+ , 1], 633 [$(M - \text{Cp}^*)^+$, 2], 556 [$(M - \text{Cp}^* - \text{Ph})^+$, 5], 477 [$(M - \text{Cp}^* - 2\text{PhH})^+$, 7], 399 [$(M - \text{Cp}^* - 3\text{PhH})^+$, 3], 276 [Ph_3SiOH , 24], 199 [Ph_2SiOH , 90].

$(\text{C}_5\text{Me}_5)\text{TiCl}(\text{O}_2\text{C}_6\text{H}_4)$ (**5**)

A solution of 0.17 g (1.38 mmol) of $\text{Li}_2\text{O}_2\text{C}_6\text{H}_4$ in 30 ml of diethyl ether was added dropwise to 0.40 g (1.38 mmol) of Cp^*TiCl_3 in 30 ml of the same solvent and the solution was stirred overnight. It was then filtered and concentrated, some hexane was added, and the solution kept at -30°C to give red crystals of **5** in 93% yield. Analysis: found: C, 58.6; H, 5.5. $\text{C}_{16}\text{H}_{19}\text{ClO}_2\text{Ti}$ calcd.: C, 58.8; H, 5.8%.

$(\text{C}_5\text{Me}_5)\text{TiCl}(\text{O}_2\text{C}_6\text{H}_3^t\text{Bu})$ (**6**)

This was prepared in the same way as **5** from 0.18 g (1.036 mmol) of $\text{Li}_2\text{O}_2\text{C}_6\text{H}_3\text{-}4\text{-}^t\text{Bu}$ and 0.30 g (1.036 mmol) of Cp^*TiCl_3 . Yield 70%. Analysis: found: C, 62.4; H, 7.5. $\text{C}_{20}\text{H}_{27}\text{ClO}_2\text{Ti}$ calcd.: C, 62.8; H, 7.1%.

$(\text{C}_5\text{Me}_5)\text{TiMe}(\text{OSiPh}_3)_2$ (**7**)

A solution of 0.765 g (2.768 mmol) of triphenylsilanol and 0.316 g (1.384 mmol) of Cp^*TiMe_3 in 50 ml of hexane was refluxed for 8 h, then allowed to cool to room temperature, concentrated to ca. 20 ml and kept at -20°C to give yellow crystals of **7** in 95% yield. Analysis: found: C, 74.9; H, 6.5. $\text{C}_{47}\text{H}_{48}\text{O}_2\text{Si}_2\text{Ti}$ calcd.: C, 75.4; H, 6.5%.

$(\text{C}_5\text{Me}_5)\text{TiMe}_2(\text{acac})$ (**8**)

A solution of 0.147 g (1.470 mmol) of acetylacetone in 10 ml of hexane was added dropwise to 0.335 g (1.470 mmol) of Cp^*TiMe_3 in 50 ml of hexane and the mixture was stirred for 2 h then concentrated under vacuum to half its volume and kept at -30°C for 24 h. The yield of orange **8** was 90%. Analysis: found: C, 65.9; H, 9.2. $\text{C}_{16}\text{H}_{27}\text{O}_2\text{Ti}$ calcd.: C, 65.4; H, 9.0%. Molecular weight: found 313, calcd. 312.03.

$(\text{C}_5\text{Me}_5)\text{TiCl}_2(\text{acac})$ (**9**)

This was prepared from 0.186 g (1.86 mmol) of acetylacetone and 0.50 g (1.86 mmol) of $\text{Cp}^*\text{TiCl}_2\text{Me}$ in dichloromethane in the way described for **8**. The yield of orange **9** was 80%. Analysis: found: C, 51.2; H, 6.1. $\text{C}_{15}\text{H}_{24}\text{Cl}_2\text{O}_2\text{Ti}$ calcd.: C, 51.0; H, 6.3%. Molecular weight: found 344, calcd. 353.2.

$[(\text{C}_5\text{Me}_5)\text{Ti}(\text{acac})\text{O}]_2$ (**10**)

To a stirred solution of 0.46 g (1.47 mmol) of **8** in 30 ml of hexane was added 0.026 ml (1.47 mmol) of degassed water. After 2 h a yellow solid began to separate and the solution turned yellow-greenish. After 18 h the solid **10** was filtered off (yield 65%). Analysis: found: C, 60.1; H, 7.8. $\text{C}_{30}\text{H}_{48}\text{O}_6\text{Ti}_2$ calcd.: C, 60.4; H, 7.4%. Molecular weight: found 597, calcd. 596.5.

Table 4

Crystal and experimental data for the X-ray structure determinations of compound **3**

| | |
|---|---|
| <i>Crystal data</i> | |
| Formula | C ₁₈ H ₂₄ Cl ₂ OTi |
| Crystal habit | prismatic |
| Symmetry | orthorhombic <i>Pnma</i> |
| Crystal colour | Red |
| Unit cell determination | least-squares fit from 25 reflections ($\theta < 25^\circ$) |
| Unit cell dimensions | 15.930(1), 14.587(1), 8.011(1) Å |
| Packing: V (Å ³); Z ; D_c (g cm ⁻³) | 1861.5; 4; 1.34 |
| M ; $F(000)$; μ (cm ⁻¹) | 375.2; 784; 7.43 |
| <i>Experimental data technique</i> | |
| | four-circle diffractometer Enraf–Nonius CAD4 with bisecting geometry; graphite oriented monochromator, Mo- K_α , ω/θ scans |
| Number of reflexions: | |
| independent | 3097 |
| observed | 2209 ($3\sigma(I)$) criterion |
| Range of hkl | 0 20 0 22 0 11 |
| Standard reflections | 2 reflections every 100 reflections, no variation |

Crystallographic structural determination

Crystallographic and experimental details for the X-ray crystal structure determination are given in Table 4. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structures were solved by a combination of direct methods and Fourier synthesis.

The structure of **3** was refined (on F) by full-matrix least-squares calculations. All the non-hydrogen atoms were refined anisotropically. In the later stages of refinement the hydrogen atoms were included in calculated positions with thermal parameters equivalent to those of the atoms to which they are attached. Final values of $R = 0.034$ and $R_w = 0.032$ (unit weights for all observed reflections) were obtained.

Anomalous dispersion corrections and atomic scattering factors were taken from International Tables [7]. Calculations were performed with the SPD package [8] and the programs MULTAN [9] and DIRDIFF [10] on a Microvax II computer.

Acknowledgements

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