



Silyl and siloxanediyl cyclopentadienyl titanium and zirconium complexes: synthesis and reactivity.

X-ray molecular structure of $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\mu\text{-OH})\}(\mu\text{-Cl})\text{Cl}_2]_2^\dagger$

Santiago Ciruelos, Tomás Cuenca,* Rafael Gómez, Pilar Gómez-Sal,‡ Antonio Manzanero,† and Pascual Royo

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Spain

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Abstract—Chloro(dimethyl)silyl- η^5 -cyclopentadienyl group 4 metal complexes of the type $[\text{M}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$ ($\text{M} = \text{Ti}$ **1**, Zr **2**) react with thallium salts $\text{Tl}(\text{C}_5\text{H}_4\text{R})$ ($\text{R} = \text{H}$, SiMe_3) to give mixed dicyclopentadienyl derivatives $[\text{M}(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_2]$, ($\text{M} = \text{Ti}$, $\text{R} = \text{H}$ **3**, $\text{R} = \text{SiMe}_3$ **4**; $\text{M} = \text{Zr}$, $\text{R} = \text{H}$ **5**, $\text{R} = \text{SiMe}_3$ **6**) in high yield. Hydrolysis of complexes **3** and **4** affords the dinuclear complexes $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}_2]_2\{\mu\text{-}[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)_2\text{O}]\}$ ($\text{R} = \text{H}$ **7**, $\text{R} = \text{SiMe}_3$ **8**) containing a siloxanyl bridge, by elimination of two equivalents of HCl. Reactions of complexes **1** with hydroxo containing reagents such as anhydrous LiOH and $\text{SiPh}_2(\text{OH})_2$ give the derivatives $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_2(\mu\text{-O})]$, **9** and $[\text{Ti}(\mu\text{-}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{OSiPh}_2\text{-}\eta^1\text{-O}))\text{Cl}_2]$, **10** identified by analytical, spectrometric and spectroscopic data. Treatment of analogous complex **2** with water produces the dimeric monocyclopentadienyl zirconium trichloride adduct $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{OH})\text{Cl}_3]_2$, **11**. Compound **11** has been characterized by X-ray crystallography. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: titanium; zirconium; siloxanediyl cyclopentadienyl; hydroxide.

Cyclopentadienyl transition metal complexes have been the subject of considerable interest for many years due to their synthetic and catalytic applications [1]. Particularly relevant has been the development of new dicyclopentadienyl group 4 metal derivatives because of their application as catalysts in homogeneous polymerization of α -olefins [2]. For this reason, a large number of such complexes with variously functionalised substituents on the cyclopentadienyl rings have been synthesized and spectroscopically and structurally characterized [3].

The aim of combining the properties of the homogeneous and heterogeneous catalysts [4], extending and improving the industrial applications of these compounds, has promoted a growing interest in the

study of transition metal complexes based on functionalized cyclopentadienyl ligands allowing their attachment to organic polymers and inorganic surfaces. Several approaches have been studied. Polysiloxanes have been investigated as useful polymers for supporting organometallic complexes [5]. Metallocene derivatives containing silyl groups in the side chain of the cyclopentadienyl ligand have also been synthesized and used as models, either by anchoring them to organic or inorganic substrates, or by polymerising them to organometallic polymers [6].

Chlorosilyl- η^5 -cyclopentadienyl group 4 metal complexes are good candidates to prepare supported catalysts using the Si—Cl bond as a reactive site [7]. We have previously reported chloro(dimethyl)silyl- η^5 -cyclopentadienyl group 4 metal derivatives $[\text{M}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$ ($\text{M} = \text{Ti}$ **1**, Zr **2**) [8] and their reactions with amines and amides. In this paper, we describe the synthesis and reactivity of these and other new dicyclopentadienyl complexes of titanium and zirconium with different hydroxo containing reagents

* Author to whom correspondence should be addressed.

† Dedicated to Prof. W. A. Herrmann on the occasion of his 50th birthday.

‡ X-ray diffraction studies.

tinguishing the chelating and the bridging coordination modes of the cyclopentadienyl ligands bridged by silyl groups [13,14]. The lower value of $\Delta\delta$ observed for $\text{Ti}[\mu\text{-}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{O}\}_2\text{O}]\text{Cl}_2$ can be attributed to the large interannular bridge angle formed by the two cyclopentadienyl rings and the metal centre, which induces a relaxation of the constrained environment of the metal [13]. These electronic and steric dispositions shown by the *ansa*-derivatives having large interannular bridges are similar to those found for the unbridged counterparts with substituted cyclopentadienyl ligands. In both types of complexes similar values of $\Delta\delta$ have been obtained indicating, in this case, that this spectroscopic parameter cannot be used to distinguish between the chelating and the bridging disposition of the dicyclopentadienyl ligand. However, the relative chemical shifts of the bridgehead carbon of the cyclopentadienyl rings could be used to distinguish between the two types of coordination. It has been observed that in chelating compounds, this resonance appeared at fields higher than the proximal and distal carbon resonances of the same ring [13], while for a bridging coordination mode, in dinuclear derivatives [11a,14] or for unbridged mononuclear substituted metallocene analogues [15], the reverse was observed. This feature has been explained as the result of a redistribution of the π -electron density of the ring in the *ansa*-metallocene caused by the bridge and the presence of the silicon atom [13a], resulting in shielding the C_{ipso} atom but deshielding the remaining ring carbon atoms. In contrast, complexes with an interannular hydrocarbon link do not present this spectroscopic behaviour for the C_{ipso} atom [16]. The ^{13}C NMR spectrum of complex **7** exhibits two signals at δ 121.0 and 129.2 assigned to the distal and proximal carbons of the bridging cyclopentadienyl rings and one resonance of lower intensity at δ 129.3 attributed to the C_{ipso} . These data are in agreement with a bridging coordination mode of the $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)\text{O}]^{2-}$ fragment in **7**. An analogous result was observed for complex **8**. The same spectroscopic characteristics [11a] have been found in other complexes containing shorter bridges like those with the $[(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2]^{2-}$ fragment. The IR spectra for complexes **7** and **8** show no absorptions due to hydroxo groups or Ti—O—Ti linkage. In addition, the mass spectra of the two compounds are in agreement with their dinuclear formulation.

Reactions of monocyclopentadienyl derivatives with hydroxo containing reagents

We have previously reported that both Si—Cl and Ti—Cl bonds in compound **1** are simultaneously involved in reactions with water and amines, whereas reactions with nucleophilic Grignard reagents or highly polar lithium amides take place selectively at the Ti—Cl bond [8,17]. In order to obtain additional information about this different reactivity we have studied the reaction of **1** with $\text{SiPh}_2(\text{OH})_2$ and LiOH.

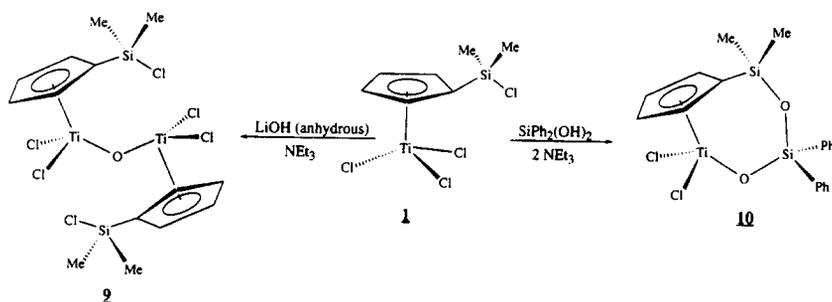
Complex **1** reacts with one equiv. of $\text{SiPh}_2(\text{OH})_2$ in the presence of two equiv. of NEt_3 to afford the mononuclear derivative $\text{Ti}[\mu\text{-}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{OSiPh}_2\text{-}\eta^1\text{-O})]\text{Cl}_2$ **10**, characterized by its analytical and spectroscopic data. This reaction involves both Si—Cl and Ti—Cl bonds as does the similar reaction with water. Treatment of **1** with anhydrous LiOH in a 1 : 1 molar ratio in the presence of one equiv. of dry NEt_3 gives the new oxo derivative $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_2](\mu\text{-O})$, **9** as yellow crystals in a 42% yield and a white precipitate of $\text{HCl}\cdot\text{NEt}_3$, on the basis of their analytical and spectroscopic data.

The formation of the dinuclear complex $[\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-O}\}_2\text{Cl}_2]_2$ obtained by hydrolysis of **1** [8] or the recently reported compound $(\text{TiCl}_2)_2(\mu\text{-O})\{\mu\text{-}[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)_2\text{O}]\}$ [12] is not detected in this reaction. The synthesis of the dinuclear complex **9** suggests that the reaction of **1** with LiOH proceeds with intermolecular elimination of HCl from the Ti—Cl bonds. In contrast, the mononuclear "constrained geometry derivatives" $\text{Ti}[\mu\text{-}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-NR})]\text{Cl}_2$ [17] are obtained in the reaction of **1** with LiNHR, involving the formation of the amidotitanium derivative $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})(\text{Cl}_2)(\text{NHR})]$ and further intramolecular HCl elimination from the silicon-bonded chlorine of the same molecule. In addition, the IR spectrum of **9** shows a broad absorption band at 798 cm^{-1} attributed to a Ti—O—Ti fragment [18] and its mass spectrum is consistent with a dinuclear structure.

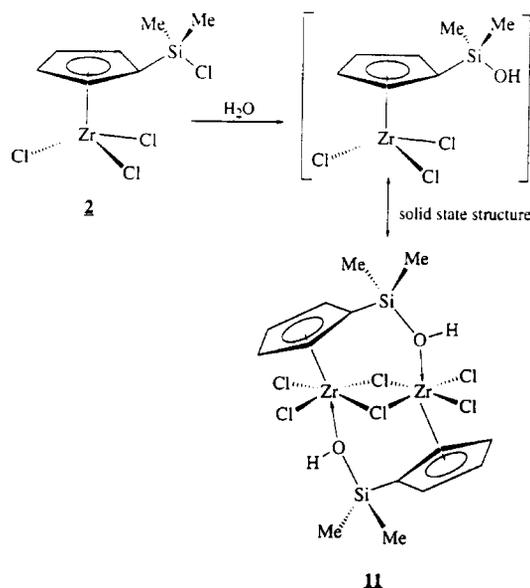
However, the reaction of the zirconium complex **2** with one equiv. of water under the same conditions has been described to give a white solid, insoluble in all common solvents [8]. The IR spectrum for this substance shows an absorption band at 3604 cm^{-1} attributed to the presence of a Si—OH group [19] and the NMR data are not reported because of its lack of solubility in the most common deuterated solvents. By using the method described in the experimental section we were successful in isolating single crystals of this compound suitable for definitive characterization by diffraction methods. The structure corresponds to a dimer of the monocyclopentadienyl zirconium trichloride unit $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\mu\text{-OH})\}(\mu\text{-Cl})\text{Cl}_2]_2$, **11** with both zirconium atoms bridged by two chlorines and the OH groups. This result confirms that the Si—Cl bonds of the chlorodimethylsilyl cyclopentadienyl substituted zirconium complex **2** react selectively with water, in contrast with the unselective hydrolysis observed for complex **1** [8].

*Description of the crystal structure of $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\mu\text{-OH})\}(\mu\text{-Cl})\text{Cl}_2]_2$, **11***

Figure 1 shows an ORTEP view of **11** along with the numbering scheme used. Selected bond lengths and angles with their standard deviations are listed in Table 1. The X-ray determination shows **11** as a dimer of two $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{OH})\text{Cl}_2]$ units. The metal



Scheme 2.



Scheme 3.

centre can be considered as having a distorted octahedral environment, surrounded by a silyl substituted cyclopentadienyl ligand that occupies one coordination site, four chlorine atoms defining the equatorial positions (two of which act as terminal atoms and the other two bridging the adjacent zirconium atoms) and a hydroxy group bound to the silicon of the neighbouring silyl group of the other cyclopentadienyl unit in a *trans* position with respect to the ring. The metal atom is located above the plane defined by its chloride substituents (0.5785 Å). The Zr—Cl terminal distances are slightly different (Zr(1)—Cl(2), 2.435(2) Å and Zr(1)—Cl(3), 2.456(2) Å) despite the symmetry of the molecule. The dimer is centrosymmetric and exhibits the trapezoidal $[\text{Zr}_2(\mu\text{-Cl})_2]$ fragment found in analogous monocyclopentadienyl zirconium derivatives [20] and other related cyclopentadienyl free ligand complexes [21]. The two Zr—Cl bridging distances are longer than the terminal Zr—Cl bonds and remain inequi-

valent (Zr(1)—Cl(1), 2.612(1) Å and Zr(1)—Cl(1a), 2.646(1) Å).

The Zr—Cp(centroid) bond distance of 2.216 Å can be compared to the values reported for other similar complexes such as 2.19 Å for $\text{Zr}(\text{C}_5\text{H}_5)\text{Cl}_3$ [20a] or 2.20 Å for $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$ [22] but is smaller than in the related complex $\text{Zr}[\eta^5\text{-C}_5\text{H}_5\text{-1,3-(SiMe}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2]\text{Cl}_3$ (2.260 Å) [23]. The loss of the polymeric structure found in $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3$ must be attributed to the formation of the hydroxo adduct, *trans* to the cyclopentadienyl group. The Zr(1)—O(1) bond distance of 2.321(4) Å is comparable to that found in other monocyclopentadienyl zirconium adduct complexes such as $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot 2\text{THF}$ (2.393 and 2.314 Å) or $\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Cl}_3 \cdot 2\text{THF}$ (2.377 and 2.310 Å) [24], although higher than that observed for terminal hydroxo complexes such as $\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{OH})_2$ (1.982 and 1.975 Å) [25] or $\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{OH})\text{Cl}$ (1.950 Å) [25].

If the centroid of the silyl-substituted ring is considered as a coordination site bonded to zirconium, the structure of **11** can be viewed as showing an eight-membered ring (Zr—O—Si—Cp)₂ with two inter-anular Zr—Cl—Zr connections (Fig. 2A). This eight-membered core has also been observed in other titanium and zirconium compounds: $[\text{TiCl}_2\{\mu\text{-}(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{O})\}]_2$ [8] (Fig. 2B) and $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\mu\text{-O})\}\text{Cl}_2\{\text{H}_2\text{NCH}(\text{Me})\text{Ph}\}]_2$ [17] (Fig. 2C). The zirconium derivative (A) exhibits a “chair conformation” similar to that found in the titanium compound (B), with the main plane of this chair conformation perpendicular to the plane defined by the zirconium and the bridged chlorine atoms (Fig. 3). The zirconium compound (C) shows a planar disposition for the cycle. The difference between the (M—O—Si—Cp)₂ cores displayed in A and B is a variation in those atoms located out of the plane. In compound **11** (A), the silicon atoms are located at ± 0.6101 Å from the plane defined by the rest of the atoms, whereas in the structure B the cyclopentadienyl rings are located out of the plane. The structure C can also be considered as two lateral Zr—Cp—Si—O “oxazirconacycle” rings connected by a central $[\text{Zr}(\mu\text{-O})_2]$ ring with the angle values substantially away from linearity ($\alpha = 141.6^\circ$ and $\beta = 108.2^\circ$). The

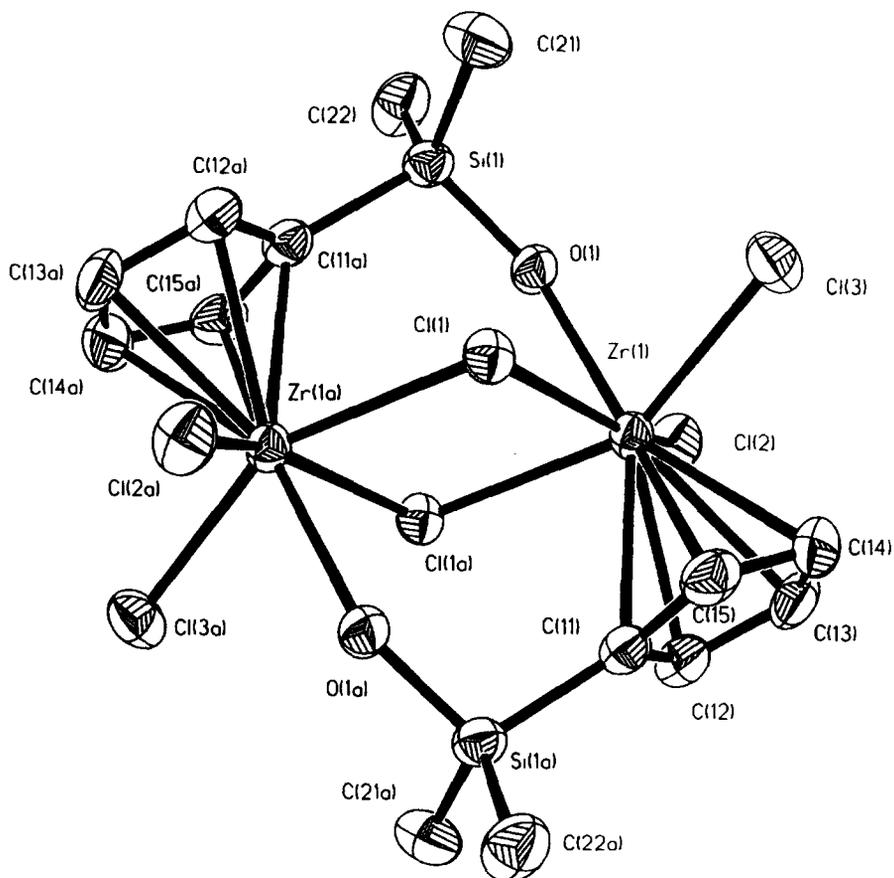


Fig. 1. ORTEP view of the molecular structure of $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\mu\text{-OH})\}(\mu\text{-Cl})\text{Cl}_2]_2$ **11** with the atom-numbering scheme.

Table 1. Selected bond lengths [Å] and angles [°] for **11**

| | | | |
|--------------------|-----------|--------------------|-----------|
| Zr(1)—O(1) | 2.321(4) | Zr(1)—Cl(2) | 2.435(2) |
| Zr(1)—Cl(3) | 2.456(2) | Zr(1)—C(12) | 2.489(6) |
| Zr(1)—C(11) | 2.506(5) | Zr(1)—C(13) | 2.520(6) |
| Zr(1)—C(15) | 2.525(6) | Zr(1)—C(14) | 2.548(6) |
| Zr(1)—Cl(1) | 2.612(1) | Zr(1)—Cl(1a) | 2.646(1) |
| Cl(1)—Zr(1a) | 2.646(1) | Si(1)—O(1) | 1.697(4) |
| Si(1)—C(22) | 1.846(6) | Si(1)—C(21) | 1.838(7) |
| Si(1)—C(11a) | 1.868(6) | C(11)—C(12) | 1.419(8) |
| C(11)—C(15) | 1.413(8) | C(11)—Si(1a) | 1.868(6) |
| C(12)—C(13) | 1.405(8) | C(13)—C(14) | 1.382(10) |
| C(15)—C(14) | 1.404(9) | Zr(1)—Cp(1) | 2.216 |
| O(1)—Zr(1)—Cl(2) | 76.39(10) | O(1)—Zr(1)—Cl(3) | 77.79(10) |
| Cl(2)—Zr(1)—Cl(3) | 96.99(6) | O(1)—Zr(1)—Cl(1) | 77.03(10) |
| Cl(2)—Zr(1)—Cl(1) | 151.60(5) | Cl(3)—Zr(1)—Cl(1) | 87.00(5) |
| O(1)—Zr(1)—Cl(1a) | 75.67(10) | Cl(2)—Zr(1)—Cl(1a) | 85.72(5) |
| Cl(3)—Zr(1)—Cl(1a) | 151.87(5) | Cl(1)—Zr(1)—Cl(1a) | 78.17(4) |
| Zr(1)—Cl(1)—Zr(1a) | 101.83(4) | O(1)—Si(1)—C(22) | 106.0(3) |
| O(1)—Si(1)—C(21) | 110.9(3) | C(22)—Si(1)—C(21) | 112.3(3) |
| Si(1)—O(1)—Zr(1) | 141.4(2) | O(1)—Zr(1)—Cp(1) | 178.76 |
| Cl(1)—Zr(1)—Cp(1) | 103.09 | Cl(1a)—Zr(1)—Cp(1) | 103.13 |
| Cl(2)—Zr(1)—Cp(1) | 103.27 | Cl(3)—Zr(1)—Cp(1) | 103.45 |

Symmetry transformations used to generate equivalent atoms: $-x, -y+2, -z+1$.
Cp(1) is the centroid of C11 C12 C13 C14 C15.

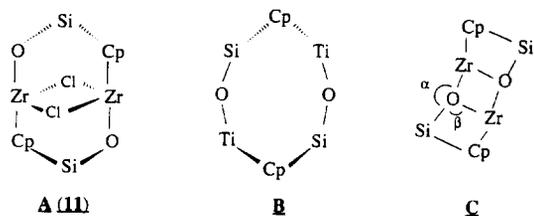


Fig. 2. Comparison of the eight-membered cores defined in the compounds $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\mu\text{-OH})\}(\mu\text{-Cl})\text{Cl}_2]_2$ (*A*, **11**), $[\text{TiCl}_2\{\mu\text{-}(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{O})\}_2]$ (*B*) and $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2(\mu\text{-O})\}\text{Cl}_2\{\text{H}_2\text{NCH}(\text{Me})\text{Ph}\}_2]$ (*C*).

O(1)—Zr(1)—Cp(1) angle in *A* is almost linear (178.76°) whereas the value of the Si(1)—O(1)—Zr(1) and C(11a)—Si(1)—O(1) angles are $141.4(2)$ and $108.4(6)^\circ$ respectively. The Zr(1)—Zr(1a) distance in compound **11** is 4.081 \AA , larger than that found in the compound *C* (3.597 \AA). The Ti—O—Si angle in the titanium compound *B* is larger (160.2°) than that found in *C* but smaller than that found in *A*. The metallic environment has a direct influence on the difference between these structures. Whereas the coordination around the titanium atom in *B* is pseudotetrahedral, the zirconium atom in *A* and *C* shows a pseudooctahedral environment and they adopt a disposition which allows their connection through the chlorine or oxygen bridges.

The formation of the adduct in complex **11** is related

to the structure of the starting material **2**, in which the hydroxo group has probably been replaced by a chlorine atom. Therefore, we tentatively assume a dimeric structure in the solid state for complex **2**, instead of a polymeric structure that may be envisaged for less hindered substituted cyclopentadienyl ligands.

EXPERIMENTAL

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glove box model HE-63. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium-potassium alloy for hexane and P_2O_5 for dichloromethane). $\text{SiPh}_2(\text{OH})_2$ (Aldrich) and anhydrous LiOH (Ventron) were commercially obtained and used without further purification. NEt_3 (Fluka) was distilled from sodium before use and stored over 4 \AA molecular sieves. $\text{Ti}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl}\}\text{Cl}_3$, **1** [8], $\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl}\}\text{Cl}_3$, **2** [8], $\text{Ti}(\text{C}_5\text{H}_5)$ [26] and $\text{Ti}(\text{C}_5\text{H}_4\text{SiMe}_3)$ [27] were prepared by known procedures. C, H and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. Electron impact (EI) mass spectra were recorded at 70 eV on a Hewlett-Packard 5988A spectrometer. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer using KBr pellets; only selected MS and IR data are reported. NMR spectra, measured at 25°C , were recorded on a Varian Unity FT-300 (^1H

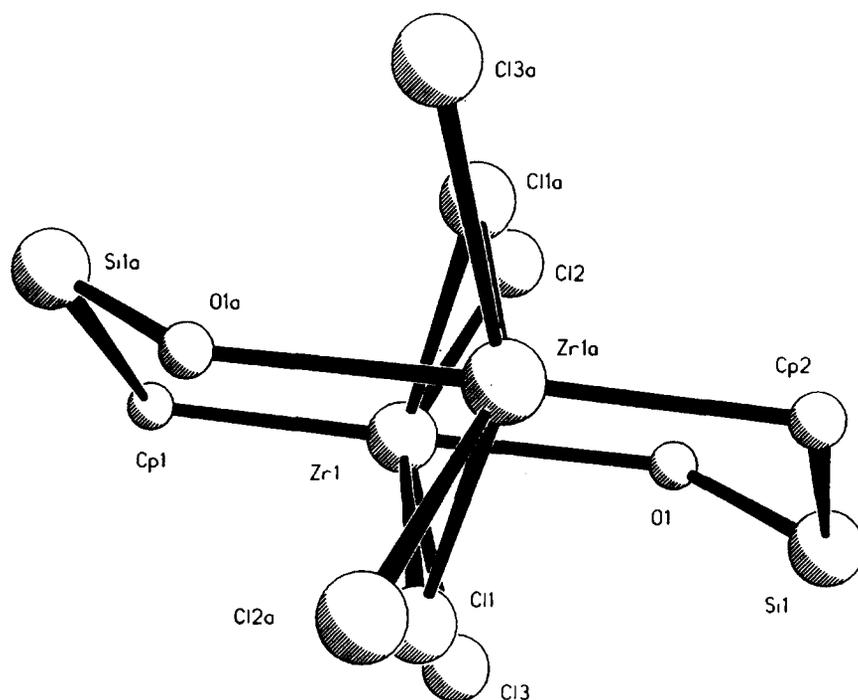


Fig. 3. "Chair-conformation" view of the eight-membered core found in compound **11**.

NMR at 300 MHz, ^{13}C NMR at 75 MHz) spectrometer and chemical shifts are referenced to TMS via residual protons (^1H) or the carbon resonances (^{13}C) of the solvent.

Synthesis of $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_2$ (**3**)

A mixture of **1** (4.7 g, 15.1 mmol) and $\text{Ti}(\text{C}_5\text{H}_5)$ (4.1 g, 15.2 mmol) in 100 ml of toluene was refluxed for 5 h. A deep red solution was formed. The reaction mixture was filtered and the residue washed with dichloromethane (2×25 ml). The solutions were combined and solvent was removed *in vacuo*. The resulting crystalline solid was washed with cold hexane (2×50 ml) and dried under vacuum to obtain a red powder identified as **3** (4.2 g, 12.3 mmol, 82% yield). Anal. cald. for $\text{C}_{12}\text{H}_{15}\text{Cl}_3\text{SiTi}$: C: 42.20; H: 4.43. Found: C: 42.84; H: 4.36. ^1H NMR (CDCl_3): δ 0.74 (s, 6H, SiMe_2); 6.59 (s, 5H, C_5H_5); 6.61 (m, 2H, C_5H_4); 6.89 (m, 2H, C_5H_4). ^1H NMR (C_6D_6): δ 0.76 (s, 6H, SiMe_2); 5.65 (m, 2H, C_5H_4); 5.92 (s, 5H, C_5H_5); 6.42 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 3.2 (SiMe_2); 119.7, 129.0 ($\text{C}_{2,5}$, C_5H_4); 120.6 (C_5H_5); 128.0 (C_{ipso} , C_5H_4). MS: m/z [assignment, R_{int} (%)]: 342 [M^+ , 2]; 327 [($\text{M}-\text{CH}_3$) $^+$, 1]; 305 [($\text{M}-\text{Cl}$) $^+$, 12]; 277 [($\text{M}-\text{C}_5\text{H}_5$) $^+$, 100]; 122 [($\text{C}_5\text{H}_4\text{SiMe}_2$) $^+$, 92].

Synthesis of $\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_2$ (**4**)

The same procedure described to prepare complex **3** using **1** (3.8 g, 12.2 mmol) and $\text{Ti}(\text{C}_5\text{H}_4\text{SiMe}_3)$ (4.2 g, 12.3 mmol) gave **4** as a reddish-brown powder (4.5 g, 10.9 mmol, 89% yield). Anal. cald. for $\text{C}_{15}\text{H}_{23}\text{Cl}_3\text{Si}_2\text{Ti}$: C: 43.54; H: 5.60. Found: C: 43.41; H: 5.50. ^1H NMR (CDCl_3): δ 0.27 (s, 9H, SiMe_3); 0.75 (s, 6H, SiMe_2); 6.56 (m, 2H, C_5H_4); 6.60 (m, 2H, C_5H_4); 6.81 (m, 4H, C_5H_4). ^1H NMR (C_6D_6): δ 0.28 (s, 9H, SiMe_3); 0.80 (s, 6H, SiMe_2); 5.74 (m, 2H, C_5H_4); 5.84 (m, 2H, C_5H_4); 6.37 (m, 2H, C_5H_4); 6.47 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 0.0 (SiMe_3); 3.3 (SiMe_2); 118.2, 120.3, 129.8, 130.0 ($\text{C}_{2,5}$, C_5H_4); 128.3, 133.6 (C_{ipso} , C_5H_4). MS: m/z [assignment, R_{int} (%)]: 414 [M^+ , 3]; 399 [($\text{M}-\text{CH}_3$) $^+$, 8]; 377 [($\text{M}-\text{Cl}$) $^+$, 6]; 277 [($\text{M}-\text{C}_5\text{H}_4\text{SiMe}_3$) $^+$, 100]; 122 [($\text{C}_5\text{H}_4\text{SiMe}_2$) $^+$, 58].

Synthesis of $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_2$ (**5**)

A mixture of **2** (10.6 g, 29.8 mmol) and $\text{Ti}(\text{C}_5\text{H}_5)$ (8.1 g, 30 mmol) in 200 ml of toluene was refluxed for 5 h. A colourless solution was formed. After filtration, the residue was washed with dichloromethane (2×75 ml). The solutions were combined and solvent was removed *in vacuo*. The resulting crystalline solid was washed with cold hexane (2×75 ml) and dried under vacuum to obtain an off-white powder identified as **5** (9.6 g, 27 mmol, 84% yield). Anal. cald. for

$\text{C}_{12}\text{H}_{15}\text{Cl}_3\text{SiZr}$: C: 37.45; H: 3.93. Found: C: 37.30; H: 3.98. ^1H NMR (CDCl_3): δ 0.73 (s, 6H, SiMe_2); 6.49 (s, 5H, C_5H_5); 6.57 (m, 2H, C_5H_4); 6.79 (m, 2H, C_5H_4). ^1H NMR (C_6D_6): δ 0.67 (s, 6H, SiMe_2); 5.77 (m, 2H, C_5H_4); 5.91 (s, 5H, C_5H_5); 6.34 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 3.1 (SiMe_2); 116.3 (C_5H_5); 117.0, 125.2 ($\text{C}_{2,5}$, C_5H_4); 121.7 (C_{ipso} , C_5H_4). MS: m/z [assignment, R_{int} (%)]: 384 [M^+ , 4]; 369 [($\text{M}-\text{CH}_3$) $^+$, 1]; 349 [($\text{M}-\text{Cl}$) $^+$, 9]; 319 [($\text{M}-\text{C}_5\text{H}_5$) $^+$, 100]; 122 [($\text{C}_5\text{H}_4\text{SiMe}_2$) $^+$, 67].

Synthesis of $\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_2$ (**6**)

The same procedure described to prepare complex **5** using **2** (5.3 g, 14.9 mmol) and $\text{Ti}(\text{C}_5\text{H}_4\text{SiMe}_3)$ (5.1 g, 14.9 mmol) gave **6** as an off-white powder (5.7 g, 12.4 mmol, 84% yield). Anal. cald. for $\text{C}_{15}\text{H}_{23}\text{Cl}_3\text{Si}_2\text{Zr}$: C: 39.41; H: 5.07. Found: C: 39.84; H: 5.19. ^1H NMR (CDCl_3): δ 0.28 (s, 9H, SiMe_3); 0.73 (s, 6H, SiMe_2); 6.53 (m, 4H, C_5H_4); 6.69 (m, 2H, C_5H_4); 6.74 (m, 2H, C_5H_4). ^1H NMR (C_6D_6): δ 0.28 (s, 9H, SiMe_3); 0.73 (s, 6H, SiMe_2); 5.83 (m, 2H, C_5H_4); 5.90 (m, 2H, C_5H_4); 6.34 (m, 2H, C_5H_4); 6.41 (m, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 0.0 (SiMe_3); 3.1 (SiMe_2); 115.8, 116.5, 125.8, 126.1 ($\text{C}_{2,5}$, C_5H_4); 121.7, 127.1 (C_{ipso} , C_5H_4). MS: m/z [assignment, R_{int} (%)]: 456 [M^+ , 1]; 441 [($\text{M}-\text{CH}_3$) $^+$, 30]; 421 [($\text{M}-\text{Cl}$) $^+$, 4]; 319 [($\text{M}-\text{C}_5\text{H}_4\text{SiMe}_3$) $^+$, 41]; 122 [($\text{C}_5\text{H}_4\text{SiMe}_2$) $^+$, 100].

Synthesis of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]_2[(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)_2\text{O}]$ (**7**)

Distilled water (174 μl , 9.7 mmol) was added to 150 ml of dry toluene. This mixture was stirred for 15 h and then **3** (3.3 g, 9.7 mmol) was dissolved in portions. The reaction mixture was stirred at room temperature for 3 days. During the course of the reaction, a red crystalline solid formed which was collected by filtration, washed with both cold toluene (15 ml) and hexane (2×30 ml) and dried under vacuum at 110 $^\circ\text{C}$ for 2 h to give **7** (1.6 g, 2.5 mmol, 53% yield based on starting complex **3**). Anal. cald. for $\text{C}_{24}\text{H}_{30}\text{Cl}_4\text{OSi}_2\text{Ti}_2$: C: 45.88; H: 4.81. Found: C: 46.42; H: 4.77. ^1H NMR (CDCl_3): δ 0.35 (s, 12H, SiMe_2); 6.56 (s, 10H, C_5H_5); 6.58 (m, 4H, C_5H_4); 6.88 (m, 4H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 2.0 (SiMe_2); 120.4 (C_5H_5); 121.0, 129.2 ($\text{C}_{2,5}$, C_5H_4); 129.3 (C_{ipso} , C_5H_4). MS: m/z [assignment, R_{int} (%)]: 628 [M^+ , not observed]; 378 [($\text{M}-\text{Cp}_2\text{TiCl}_2$) $^+$, 14]; 343 [($\text{M}-\text{Cp}_2\text{TiCl}_2\text{-Cl}$) $^+$, 9]; 248 [(Cp_2TiCl_2) $^+$, 23]; 183 [(CpTiCl_2) $^+$, 100]; 122 [($\text{C}_5\text{H}_4\text{SiMe}_2$) $^+$, 41].

Synthesis of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2]_2[(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)_2\text{O}]$ (**8**)

The same procedure described to prepare complex **7** using **4** (2.9 g, 7.0 mmol) and distilled water (126 μl ,

7.0 mmol) gave **8** as a microcrystalline red solid (1.3 g, 1.7 mmol, 49% yield based on starting complex **4**). Anal. cald. for $C_{30}H_{46}Cl_4OSi_4Ti_2$: C: 46.63; H: 6.00. Found: C: 46.23; H: 5.79. 1H NMR ($CDCl_3$): δ 0.27 (s, 18H, SiMe₃); 0.35 (s, 12H, SiMe₂); 6.52 (m, 4H, C₅H₄); 6.58 (m, 4H, C₅H₄); 6.77 (m, 4H, C₅H₄); 6.81 (m, 4H, C₅H₄). 1H NMR (CD_2Cl_2): δ 0.28 (s, 18H, SiMe₃); 0.36 (s, 12H, SiMe₂); 6.55 (m, 4H, C₅H₄); 6.60 (m, 4H, C₅H₄); 6.77 (m, 4H, C₅H₄); 6.80 (m, 4H, C₅H₄). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.0 (SiMe₃); 2.1 (SiMe₂); 119.7, 120.0, 129.8, 130.2 (C₂₋₅, C₅H₄); 129.3, 133.2 (C_{ipso}, C₅H₄). MS: m/z [assignment, R_{int} (%): 772 [M⁺, not observed]; 392 {[C₅H₄SiMe₃]₂TiCl₂}⁺, 2]; 378 {[M-(C₅H₄SiMe₃)₂TiCl₂]⁺, 100]; 343 {[M-(C₅H₄SiMe₃)₂TiCl₂-Cl]⁺, 26]; 255 [(C₅H₄SiMe₃)TiCl₂]⁺, 36]; 122 [(C₅H₄SiMe₂)⁺, 38].

Synthesis of [Ti(η^5 -C₅H₄SiMe₂Cl)Cl₂](μ -O) (**9**)

A suspension of anhydrous LiOH (93 mg, 3.8 mmol) and NEt₃ (0.53 ml, 3.8 mmol) was added to a solution of **1** (1.2 g, 3.8 mmol) in 50 ml of toluene. The reaction mixture was allowed to stir at room temperature for 20 h and then filtered. Solvent was completely removed from the resulting orange-yellow solution *in vacuo* to give **10** as a yellow solid which was further purified by recrystallization from a mixture of toluene (20 ml) and hexane (40 ml) at $-40^\circ C$ (0.46 g, 0.8 mmol, 42% yield based on starting complex **1**). Anal. cald. for $C_{14}H_{20}Cl_6OSi_2Ti_2$: C: 29.55; H: 3.54. Found: C: 29.90; H: 3.52. 1H NMR ($CDCl_3$): δ 0.46 (s, 12H, SiMe₂); 7.06 (m, 4H, C₅H₄); 7.22 (m, 4H, C₅H₄). 1H NMR (C_6D_6): δ 0.29 (s, 12H, SiMe₂); 6.22 (m, 4H, C₅H₄); 6.64 (m, 4H, C₅H₄). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 1.3 (SiMe₂); 126.4, 129.1 (C₂₋₅, C₅H₄); 139.3 (C_{ipso}, C₅H₄). MS: m/z [assignment, R_{int} (%): 568 [M⁺, not observed]; 553 [(M-CH₃)⁺, 3]; 277 [(C₅H₄SiMe₂TiCl₂)⁺, 75]; 122 [(C₅H₄SiMe₂)⁺, 100]. IR (KBr, cm⁻¹): ν (Ti—O—Ti) = 798.

Synthesis of Ti(η^5 -C₅H₄SiMe₂OSiPh₂- η^1 -O)Cl₂ (**10**)

To a cooled ($-60^\circ C$) suspension of **1** (2.0 g, 6.4 mmol) in 100 ml of hexane, a suspension of SiPh₂(OH)₂ (1.39 g, 6.4 mmol) and NEt₃ (1.77 ml, 12.8 mmol) was added. The cold bath was allowed to warm to room temperature and the reaction mixture was stirred overnight and then filtered. The resulting solution was concentrated *in vacuo* to 10 ml and stored overnight at $-30^\circ C$ to obtain yellow needles identified as **9**. The product was further purified by recrystallization from hexane (1.3 g, 2.9 mmol, 45% yield). Anal. cald. for $C_{19}H_{20}Cl_2O_2Si_2Ti$: C: 50.12; H: 4.43. Found: C: 50.14; H: 4.75. 1H NMR ($CDCl_3$): δ 0.48 (s, 6H, SiMe₂); 6.75 (m, 2H, C₅H₄); 7.13 (m, 2H, C₅H₄); 7.37–7.41 (m, 6H, Ph); 7.62–7.65 (m, 4H, Ph). 1H NMR (C_6D_6): δ 0.17 (s, 6H, SiMe₂); 6.26 (m, 2H, C₅H₄); 6.50 (m, 2H, C₅H₄); 7.13–7.15 (m, 6H, Ph); 7.76–7.80 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.1

(SiMe₂); 125.3, 125.6 (C₂₋₅, C₅H₄); 128.0, 130.8, 134.2 (C_{ortho}, C_{meta}, C_{para}, Ph); 130.3 (C_{ipso}, C₅H₄); 133.0 (C_{ipso}, Ph). MS: m/z [assignment, R_{int} (%): 454 [M⁺, 13]; 439 [(M-CH₃)⁺, 23]; 377 [(M-Ph)⁺, 50]; 300 [(M-2Ph)⁺, 52].

Synthesis of [Zr(η^5 -C₅H₄SiMe₂(μ -OH))(μ -Cl)Cl₂]₂ (**11**)

Distilled water (0.1 ml, 5.6 mmol) was added to 50 ml of dry toluene. This mixture was stirred for 15 h and after this time this solution was added dropwise over a period of 2 h to a solution of **2** (2.0 g, 5.6 mmol) in 200 ml of dry toluene cooled to $0^\circ C$. The reaction mixture was stirred at room temperature overnight. During the course of the reaction, off-white crystals formed (some of them suitable for X-ray crystallographic analysis) which were collected by filtration, washed with dichloromethane (50 ml) and hexane (2 \times 50 ml) and dried under vacuum to give **11** (0.9 g, 1.3 mmol, 47% yield). Anal. cald. for $C_{14}H_{22}Cl_6O_2Si_2Zr_2$: C: 24.96; H: 3.29. Found: C: 24.49; H: 3.32. IR (KBr, cm⁻¹): ν (Si—OH) = 3604. NMR data are not reported because the product was insoluble in common deuterated solvents.

Crystal structure determination of [Zr(η^5 -C₅H₄SiMe₂(μ -OH))(μ -Cl)Cl₂]₂ (**11**)

Off-white crystals of compound **11** were obtained by crystallization from dry toluene and a suitable sized crystal was mounted in a Lindemann tube and mounted in an Enraf-Nonius CAD 4 automatic four-circle diffractometer with graphite monochromated Mo-K _{α} radiation ($\lambda = 0.71073 \text{ \AA}$). Crystallographic and experimental details are summarized in Table 2. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction correction were made. The structure was solved by direct methods (SHELXL 90) [28] and refined by least squares against F^2 (SHELXL 93) [29]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with thermal parameters equivalent to those of the atoms to which they are bonded. The hydrogen atom of the hydroxo group was not included. Calculations were carried out on an ALPHA AXP(Digital) workstation.

Supplementary material—A list of the positional parameters and their standard deviations, a complete list of bond lengths and angles, anisotropic displacement parameters, the calculated fractional coordinates of the hydrogen atoms and a list of observed and calculated structure factors are available from author T. C. upon request.

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Table 2. Crystal, experimental data and structure refinement procedures for compound 11

| | |
|--|---|
| Formula | C ₁₄ H ₂₂ Cl ₆ O ₂ Si ₂ Zr ₂ |
| Crystal habit | Prismatic |
| Color | white |
| Crystal size | 0.25 × 0.30 × 0.35 mm |
| Symmetry | Monoclinic, <i>P</i> ₂ ₁ / <i>a</i> |
| Unit cell dimensions | |
| <i>a</i> (Å) | 8.767(1) |
| <i>b</i> (Å) | 16.115(1) |
| <i>c</i> (Å) | 9.1480(1) |
| β (°) | 115.71(1) |
| <i>V</i> , Å ³ | 1164.4(2) |
| <i>Z</i> | 4 |
| <i>D</i> _{calc.} , g cm ⁻³ | 1.915 |
| <i>M</i> _w | 335.82 |
| <i>F</i> (000) | 660 |
| μ, cm ⁻¹ | 16.946 |
| Scan mode | ω/2θ 2.47 < θ < 28.18 |
| No. of reflections | |
| Measured | 3095 |
| Independent observed | 2863 (<i>R</i> _{int} = 0.0190) |
| Range of <i>h</i> , <i>k</i> , <i>l</i> | -11 < <i>h</i> < 0, -21 < <i>k</i> < 0, -12 < <i>l</i> < 12 |
| Standard reflections | 3 every 200 refl. |
| Refinement method | Full matrix least squares on <i>F</i> ² . |
| Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>)) ^a | <i>R</i> ₁ = 0.0330, <i>wR</i> ₂ = 0.0749 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0514, <i>wR</i> ₂ = 0.1117 |
| Weighting scheme | calc. ω = 1/[σ ² (<i>F</i> _o ²) + (0.0846 <i>P</i>) ² + 10.1458 <i>P</i>] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3 |
| Max peak in final diff. map (e/Å ³) | 0.975 |
| Min peak in final diff. map (e/Å ³) | -0.753 |
| Goodness-of-fit on <i>F</i> ² | 0.537 |

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \{[\sum \omega(F_o^2 - F_c^2)] / [\sum \omega(F_o^2)^2]\}^{1/2}.$$

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