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Fulvalene cyclopentadienyl titanium and zirconium(III) and -(IV) complexes. X-Ray crystal structure of $[\{Ti(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$

Ana Cano, Tomás Cuenca, Gema Rodríguez and Pascual Royo

Departamento de Química inorgánica, Universidad de Alcalá de Henares, Campus Universitario, Facultad de Ciencias, 28871 Alcala de Henares, Madrid (Spain)

Christine Cardin and Deborah J. Wilcock

Department of Chemistry, Trinity College, The University of Dublin, Dublin 2 (Ireland)

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Abstract

The reaction of the fulvalene titanium(III) hydride $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}H)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (**1**) with chlorine leads to $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (**3**) and $[\{Ti(\eta^5\text{-}C_5H_5)Cl_2\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (**4**). The reaction of **3** with azobenzene, in wet toluene, gives $[\{Ti(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (**5**) and 1,2-diphenyl hydrazine. The alkylation of **4** and the analogous zirconium complex $[\{Zr(\eta^5\text{-}C_5H_5)Cl_2\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (**2**) with $LiCH_2SiMe_3$ or $LiCH_3$ permits isolation of the tetraalkyl derivatives $[\{M(\eta^5\text{-}C_5H_5)(CH_2SiMe_3)_2\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (M = Ti (**6**); Zr (**8**)) and $[\{Ti(\eta^5\text{-}C_5H_5)(CH_3)_2\}_2(\mu\text{-}\eta^5\text{-}\eta^5C_{10}H_8)]$ (**7**). All the new fulvalene compounds were characterized by IR, and ^1H and ^{13}C NMR spectroscopy, and mass spectra and **5** by X-ray diffraction. The structure of **5** is very similar to that of the comparable Ti^{IV} compound $[\{Ti(\eta^5\text{-}C_5H_5)_2Cl\}_2(\mu\text{-}O)]$ except for the smaller Ti–O–Ti angle (159.4° against 173.81°) and a significant deviation from linearity.

1. Introduction

The activation of small molecules, reductive coupling of alkenes and alkynes, Ziegler–Natta polymerization of alkenes, as well as the formation of hydrides or metal–metal bonds have stimulated the study of complexes of low oxidation state group 4d elements [1]. The chemistry of titanium(II) and -(III) has been well developed whereas zirconium(III) is much less accessible and the reduction of zirconocene dihalides has been, for years, a tempting goal. Recently we have demonstrated that access to, and the study of, the chemistry of low oxidation state titanium and zirconium complexes, mainly in oxidation state III, is facilitated by using fulvalene [2] and *ansa*-dimethylsilylbiscyclopentadienyl [3] as ligands. The fulvalene complexes are particularly interesting because they lead to dinuclear compounds with short contacts between both metal centres and even to slight metal–metal interactions [4]. The free rotation of the rings around the C–C bond makes possible two *cis–trans* conformations of the metal fragments with respect to the fulvalene plane, depending mainly on steric factors [5]. In addition, the fulvalene group restricts secondary reactions, such as activation of ring C–H bonds, and being less of an electron donor than the unsubstituted cyclopentadienyl group, makes the metal more electron deficient.

One of the best known fulvalene titanium derivatives is "green titanocene". Different titanium(II) species have been isolated in the reduction processes from titanocene dihalides or dialkyls, but under appropriate conditions [1] the resulting bright green product is $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}H)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (**1**). A similar zirconium complex is not known and the zirconium fulvalene derivative best characterized [2a] is $[\{Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ (**2**).

Correspondence to: Professor P. Royo.

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We report here the preparation of new titanium and zirconium fulvalene complexes starting from complexes **1** and **2** and the X-ray study by diffraction methods of the previously reported [2b] compound [{Ti(η^5-C_5H_5)Cl}$_2$(μ-O)(μ-η^5-η^5-$C_{10}H_8$)].

2. Results and discussion

2.1. *Reactions of [{Ti(η^5-C_5H_5)(μ-H)}$_2$(μ-η^5-η^5-$C_{10}H_8$)] (1) with chlorine*

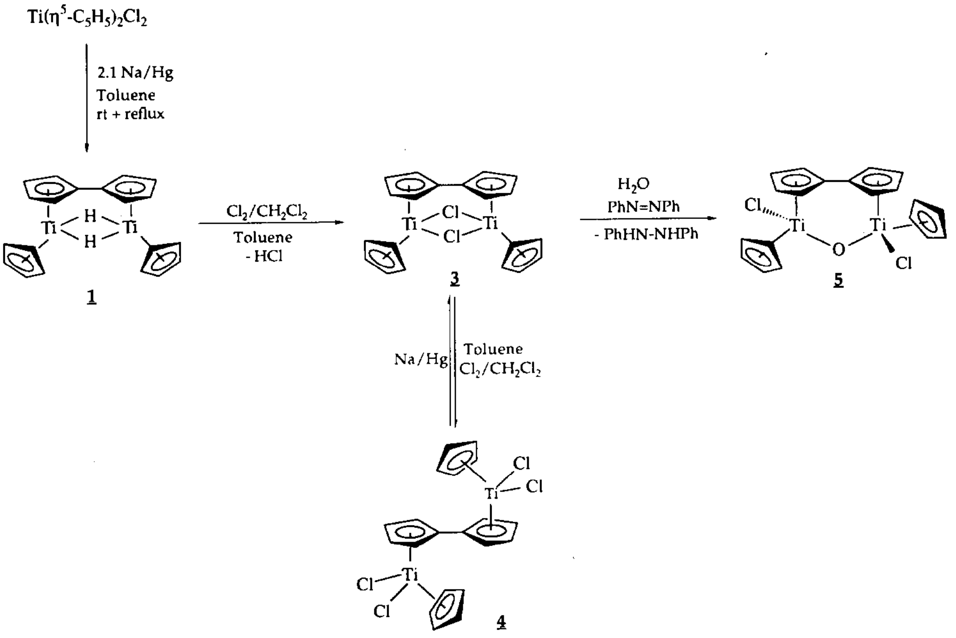
The reduction of titanocene dichloride with two equivalents of 10% sodium amalgam in toluene gives a brilliant green solution from which a crystalline compound **1** characterized [6] as [{Ti(η^5-C_5H_5)(μ-H)}$_2$(μ-η^5-η^5-$C_{10}H_8$)] can be isolated in 80% yield. This compound has also been recently prepared [1d] and characterized by X-ray diffraction methods [1e]. When a green solution of **1** is treated by dropwise addition of a solution of chlorine in dichloromethane, the colour changes immediately to purple and then rapidly to green with appearance of a green precipitate which is insoluble in most common organic solvents. After repeated washes, the green solid obtained in 70% yield was characterized as [{Ti(η^5-C_5H_5)Cl_2}$_2$(μ-η^5-η^5-$C_{10}H_8$)] (**4**). However, if the addition of chlorine is stopped while the solution is purple, this colour remains and on concentration it gives red purple crystals of **3**, identified as the previously reported [7] titanium(III) complex [{Ti(η^5-C_5H_5)(μ-Cl)}$_2$(μ-η^5-η^5-$C_{10}H_8$)].

Being insoluble in organic solvents **4** cannot be characterized by NMR spectroscopy. This lack of solubility is similar to that of the similar zirconium derivative [2d]. However the analogous pentamethycyclopentadienyl complex [8] is more soluble and its ^{1}H NMR spectrum can be obtained. The IR spectrum of **4** between 600 and 200 cm^{-1} is almost identical to that of titanocene [9], the most remarkable difference being the absorption due to the asymmetric δ(C–H) which gives bands at 1004 and 1015 cm^{-1} for titanocene, displaced and more widely spaced at 1011 and 1063 cm^{-1} for **4**. The mass spectrum of **4** confirms its dinuclear nature and the analysis agrees exactly with its formulation. From these data and from steric considerations, a *trans* conformation of pseudotetrahedral metal fragments bonded to each fulvalene cyclopentadienyl ring is postulated.

The reaction of **4** with one equivalent of sodium amalgam is an alternative method of obtaining **3** in 80% yield.

When **3** is treated with azobenzene in toluene, a yellow orange solution is obtained which, after concentration, gives the reported [2b] μ-oxo-complex [{Ti(η^5-C_5H_5)Cl}$_2$(μ-O)(μ-η^5-η^5-$C_{10}H_8$)] **5** and 1,2-diphenyl hydrazine, which was recovered from the solution and identified by ^{1}H NMR spectroscopy. A μ-hydrazido-complex, probably an intermediate, whose hydrolysis by adventitious traces of water leads to **5**, could not be isolated; this reaction is being further studied.

The nature of this previously reported [2b] μ-oxo-



Scheme 1

TABLE 1. Fractional atomic co-ordinates (×10^4) for $C_{20}H_{18}Cl_2OTi_2 \cdot 0.5C_7H_7$ [a]

Atom	x	y	z
Ti(1)	1238(1)	279(1)	3230(1)
Cl(1)	1213(2)	1084(2)	4776(2)
O(1) [b]	0	550(5)	2500
C(1)	1429(7)	1286(10)	1868(7)
C(2)	2158(7)	564(9)	2166(8)
C(3)	2715(7)	864(11)	3106(9)
C(4)	2333(9)	1768(11)	3420(8)
C(5)	1518(8)	2035(9)	2639(10)
C(6)	486(5)	−1526(6)	2872(6)
C(7)	1314(6)	−1545(7)	2609(7)
C(8)	2082(6)	−1451(7)	3531(7)
C(9)	1740(6)	−1305(7)	4321(6)
C(10)	744(6)	−1341(6)	3915(6)
C(11)	210(11)	4031(12)	−107(12)
C(13)	−267(11)	3844(12)	579(12)
C(12)	−646(11)	4729(12)	953(12)
C(11A)	−547(11)	5801(12)	640(12)
C(13A)	−70(11)	5988(12)	−47(12)
C(12A)	309(11)	5103(12)	−420(12)

[a] Atoms were refined with a site occupation factor of 0.5 and a common isotropic U value which refined to 0.0808(25).

[b] O(1) lies on the special position with point symmetry 2.

complex has been confirmed by X-ray diffraction studies.

2.2. *Structure of* $[\{Ti(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ *(5)*

An ORTEP view of **5** is shown in Fig. 1, together with the atomic labelling scheme. The atomic coordinates for non-hydrogen atoms are shown in Table 1 and important bond lengths and angles are given in Table 2.

The coordination geometry is similar to that of the related complexes [10]. However, some different features are imposed by the presence of the fulvalene ligand [2a].

TABLE 2. Bond lengths (Å) and angles (°) [a]

Cl(1)–Ti(1)	2.384(4)
C(2)–C(1)	1.354(15)
C(5)–C(1)	1.382(15)
C(3)–C(2)	1.352(14)
C(4)–C(3)	1.376(17)
C(5)–C(4)	1.380(16)
C(7)–C(6)	1.412(12)
C(6)–C(6a)	1.483(16)
C(8)–C(7)	1.419(13)
C(9)–C(8)	1.377(12)
C(10)–C(9)	1.413(12)
O(1)–Ti(1)	1.829(4)
Ti(1)–Ti(1)	3.595(4)
Ti(1)–Ce(1)	2.081(5)
Ti(1)–Ce(2)	2.095(4)
Ti(1)–O(1)–Ti(1)	159.4(4)
O(1)–C(1)–C(2)	96.4(2)
C(5)–C(1)–C(2)	109.1(10)
C(3)–C(2)–C(1)	107.5(11)
C(4)–C(3)–C(2)	109.6(11)
C(5)–C(4)–C(3)	106.9(11)
C(4)–C(5)–C(1)	107.0(11)
C(10)–C(6)–C(7)	108.2(8)
C(8)–C(7)–C(6)	106.4(8)
C(9)–C(8)–C(7)	109.3(9)
C(10)–C(9)–C(8)	107.6(8)
C(9)–C(10)–C(6)	108.3(8)

[a] Ce(1) and Ce(2) refer to the centroids of the cyclopentadienyl and fulvalene rings, respectively.

The cyclopentadienyl and fulvalene rings are planar with mean carbon–carbon distances of 1.369 Å (Cp ring) and 1.403 Å (fulvalene ring). The minimum and maximum values of 1.352(14) Å and 1.382(15) Å for the Cp ring show less variation than those for the fulvalene ring [1.377(12) Å and 1.419(13) Å]. If the ring centroids are considered as coordination sites, the coordination geometry around titanium is a distorted tetrahedron, the other two coordination sites are occupied by the

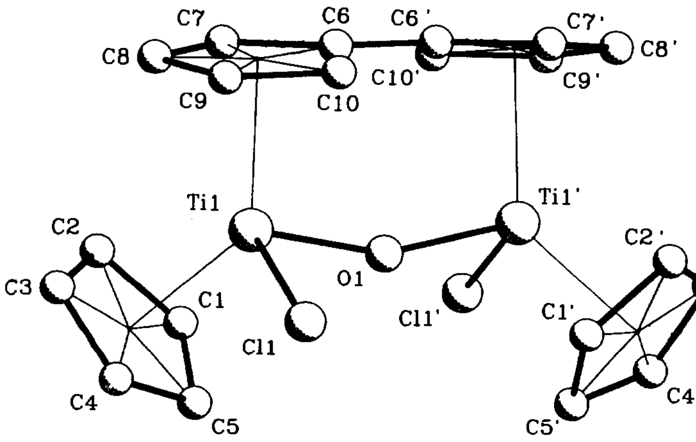


Fig. 1. ORTEP view of compound **5**.

chlorine and the oxygen atoms. The distortion from a tetrahedral symmetry is reflected in the Ce(1)–Ti–Ce(2) angle (131.9°) [Ce(1) and Ce(2) denote the centroids of the cyclopentadienyl and fulvalene rings, respectively], and the Cl–Ti–O angle (96.4°). When viewed along the line joining the centroids of the two rings (Cp and fulvalene) both rings adopt a staggered conformation, similar to $[\{Ti(\eta^5\text{-}C_5H_5)_2Cl\}_2(\mu\text{-}O)]$ [10]. The distances from the metal atom to the centroids are 2.081 Å [M—Ce(1)] and 2.095 Å [M–Ce(2)] and the Ti–Cl and Ti–O distances are 2.384 Å and 1.829 Å, respectively. The most important difference between compound **5** and the bis(cyclopentadienyl)-μ-oxo-derivative $[\{Ti(\eta^5\text{-}C_5H_5)_2Cl\}_2(\mu\text{-}O)]$ is the Ti–O–Ti angle, which is 159.4° for **5** against 173.81° in the bis(cyclopentadienyl)-μ-oxo complex. This significant deviation from linearity must be imposed by the fulvalene group.

2.3. *Alkylation of fulvalene titanium(IV) and zirconium(IV) complexes* $[\{M(\eta^5\text{-}C_5H_5)Cl_2\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ *(M = Ti (4), Zr (2)) with LiR (R =* CH_2SiMe_3 *or* CH_3*)*

The addition of 4 equivalents of LiR (R = CH_2SiMe_3 or CH_3) or MeMgCl to a suspension of **4** or **2** in toluene leads to a solution from which crystalline alkyl derivatives **6–8** can be obtained in 50–60% yield.

All compounds isolated were characterized by analysis, and by IR, NMR and mass spectroscopy.

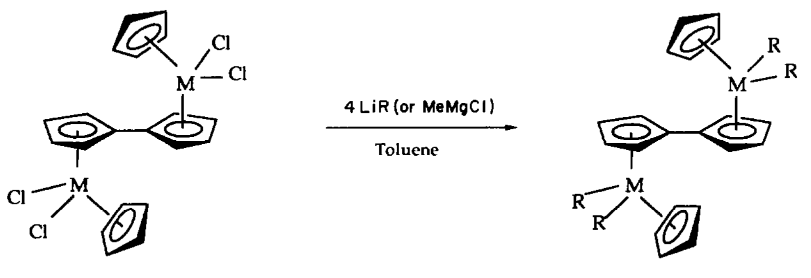
Complexes **6** and **8** are very slightly soluble in toluene, benzene, THF, dichloromethane or chloroform, but insoluble in pentane or hexane. They remain air-stable for days, but should be stored under argon or dinitrogen.

The ^1H NMR spectra of the complexes each show two pseudotriplets (δ 5.09 and 6.81 for **6**; δ 5.40 and 6.55 for **8**) characteristic of a fulvalene AA'BB' spin system and one singlet at δ 5.90 for **6** and 5.86 for **8** due to the cyclopentadienyl ring protons. This is consistent with a dinuclear structure in which the two metal fragments are located in *trans* positions, bound to each ring of a planar fulvalene. The molecule has a plane of symmetry that contains the two metal atoms and the two fulvalene C_{ipso} atoms.

The methylene protons of the CH_2SiMe_3 group are diastereotopic [11] and give rise to two doublets at δ 0.63 and 1.42 for **6** and −0.09 and 0.38 for **8**, respectively, with the same $J(H_aH_b) \simeq 10$ Hz for each complex. A similar phenomenon has been reported already [12] for $[M(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)(CH_2PPh_2)_2]$ (M = Ti or Zr) and $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Cl(CH_2PPh_2)]$ containing two different cyclopentadienyl rings, which make the metal prochiral or chiral and destroy the plane of symmetry. The $\{^1H^1H\}$ COSY 2D NMR spectrum confirms the correlation between the two H_a, H_b protons of the methylene group as well as that expected between the two fulvalene $H_{1,4}$ and $H_{2,3}$ pseudotriplets. The ^{13}C NMR spectra show the expected behaviour with one singlet at δ 81.00 for **6** and 45.8 for **8** for both equivalent methylene carbon atoms in both complexes. The mass spectra confirm the dinuclear structure.

The dimethyl compound **7** is only slightly soluble in benzene or toluene and can be stored under argon or dinitrogen for weeks without decomposition. The ^1H NMR spectrum of this compound shows the expected AA'BB' spin system for the fulvalene protons and one singlet (δ 0.14) for methyl protons. The mass spectrum confirms its dinuclear structure.

No reaction was observed for similar alkyls with R = $-pC_6H_4Me$, $-CH_2Si(Me)_2CH_2-$, $-N(SiMe_3)_2$ or $-CH_2CMe_3$, probably due to the slight solubility of **2** and **4**. Reaction of **2** with $Mg(CH_2C_6H_5)_2$ always gives $C_6H_5CH_2\text{-}CH_2C_6H_5$ as identified by ^1H NMR spectroscopy. This behaviour, which is essentially different



M= Ti(**4**),Zr(**2**)

M=Ti R=CH_2SiMe_3(**6**), CH_3(**7**)

M=Zr R=CH_2SiMe_3(**8**)

Scheme 2

for analogous metallocene derivatives, has been explained [13] as due to the intermediate formation of unstable $[\{M(\eta^5\text{-}C_5H_5)RCl\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$, which favours the elimination process to give $[M(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$.

3. Experimental section

All manipulations were performed under an inert atmosphere (dinitrogen or argon) using Schlenk and high-vacuum-line techniques or a glovebox, Pedetrol model HE-63-P. Solvents were purified by distillation from an appropriate deoxygenated drying agent. Pentane and hexane were distilled from sodium-potassium amalgam, toluene from sodium, diethyl ether and tetrahydrofuran from sodium benzophenone ketyl and chloroform and dichloromethane from P_4O_{10}. $[\{Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ [2a] and $LiCH_2SiMe_3$ [14] were prepared by reported methods. $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ was purchased from Aldrich. MeLi and MeMgCl (Aldrich) and PhN=NPh (Fluka) were obtained commercially and used without further purification. NMR spectra were recorded on Varian FT-80A and Varian Unity FT-300 instruments. ^1H and ^{13}C chemical shifts were referenced to Me_4Si. Mass spectra were recorded on a Hewlett Packard 5890 spectrometer. IR spectra were performed (Nujol mulls) on a Perkin–Elmer 883 spectrophotometer. Elemental C and H analyses were carried out on a Perkin–Elmer 240B microanalyzer.

3.1. μ-η⁵-η⁵-Fulvalenebis[(μ-chloro)(η⁵-cyclopentadienyl)titanium(III)] $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ *(3)*

3.1.1. Method A

A mixture of 4.11 g (16.6 mmol) of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ and 10% sodium (0.84 g, 36.3 mmol) amalgam was stirred in 200 ml of toluene at room temperature for 12 h. Then, the reaction mixture was heated under reflux for 3 h. A green solution was obtained. After cooling to room temperature, the solution was filtered and the residue washed with toluene until the solution was colourless. All the extracted fractions were collected and combined and the resulting solution concentrated to 50 ml. By cooling to −30°C overnight, 5 g (85% yield) of **1** (previously reported [6]) $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}H)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ was obtained as brown–green crystals.

A solution of 1.12 g (3.13 mmol) of $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}H)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ in 100 ml of toluene was treated with a stoichiometric amount of chlorine dissolved in dichloromethane at room temperature until the colour changed from green to purple. After stirring for 1 h, the solution was filtered and the solvent evaporated to dryness under vacuum. The purple residue was washed several times with diethyl ether until the solution was colourless to give 1 g (75% yield) of **3** (previously reported [7]) as a purple microcrystalline solid.

3.1.2. Method B

A suspension of 1.67 g (3.36 mmol) of $[\{Ti(\eta^5\text{-}C_5H_5)Cl_2\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ and 10% sodium (0.077 g, 3.36 mmol) amalgam was stirred in 50 ml of toluene at room temperature for 12 h. The colour slowly turned purple. The resulting solution was filtered and the residue washed several times with toluene until the solution was colourless. All the extracted fractions were collected and combined. The solution was concentrated to 20 ml and cooled to −20°C to give 1 g (70% yield) of the title microcrystalline compound **3**.

3.2. μ-η⁵-η⁵-Fulvalenebis[dichloro(η⁵-cyclopentadienyl)titanium(IV)] $[\{Ti(\eta^5\text{-}C_5H_5)Cl_2\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ *(4)*

A solution of 1.23 g (2.88 mmol) of $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ in 50 ml of toluene was treated with an excess of chlorine dissolved in dichloromethane, at room temperature. The purple solution turned green and a solid of the same colour was formed. The reaction mixture was stirred for 1 h. The solvent was evaporated to dryness under vacuum and the resulting residue was washed in order with chloroform (2 × 50 ml), tetrahydrofuran (2 × 50 ml), hexane (2 × 50 ml) and acetone (2 × 50 ml) to give 1 g (70% yield) of compound **4**.

Anal. Calc. for $C_{20}H_{18}Cl_4Ti_2$ (found): C, 48.43 (48.53); H, 3.65 (3.48) %. IR spectrum (Nujol mull): 3108 (m), 1415 (m), 1305(m), 1063(m), 1011(m), 852(s), 825(s), 605(m), 411(m), 393(m), 360(m), 304(s), 250(s), 240(m) cm^{-1}. Mass spectrum m/z 424 $([M]\text{-}2Cl)^+$.

3.3. μ-η⁵-η⁵-Fulvaleneμ-oxobis[chloro(η⁵-cyclopentadienyltitanium(IV)] $[\{Ti(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ *(5)*

A solution containing 0.60 g (3.30 mmol) of azobenzene in wet toluene was added to a solution of 1.28 g (3.02 mmol) of $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]$ in toluene. The reaction mixture was stirred for 12 h. A yellow precipitate was formed. The solvent was evaporated and the solid obtained washed with hexane. Recrystallization from toluene/hexane at −20°C gave compound **5** as an orange–yellow crystalline solid (1 g, 75% yield), identified as the previously reported [2b] compound.

3.4. μ-η^5-η^5-Fulvalenebis[{bis(trimethylsilylmethyl)}-(η^5-cyclopentadienyl)titanium(IV)] [{Ti(η^5-C_5H_5)-($CH_2SiMe_3)_2\}_2(\mu$-η^5-η^5-$C_{10}H_8$)] (6)

To a suspension of 1.17 g (2.37 mmol) of [{Ti(η^5-C_5H_5)$Cl_2\}_2$(μ-η^5-η^5-$C_{10}H_8$)] in 50 ml of toluene a solution of 0.91 g (9.72 mmol) of $LiCH_2SiMe_3$ in 20 ml of toluene was added at −20°C. The reaction mixture was warmed to room temperature. After 12 h of stirring the solution was filtered and the solvent was removed under vacuum to give an orange-yellow residue which was washed twice with hexane. Recrystallization from toluene/hexane gave 1 g (60% yield) of compound **6**.

Anal. Calc. for $C_{36}H_{62}Si_4Ti_2$ (found): C, 61.51 (61.33); H, 8.89 (8.68) %. ^{1}H NMR spectrum (300 MHz, C_6D_6, 25°C): δ 0.18 (s, 36H, MeSi), 0.63 (d, $J = 10.5$ Hz, 4H, CH_2–Si), 1.42 (d, $J = 9.53$ Hz, 4H, CH_2–Si), 5.09 (t, C_5H_4), 5.90 (s, C_5H_5), 6.81 (t, C_5H_4). ^{13}C NMR spectrum (75 MHz, C_6D_6, 25°C) :δ3.71 (MeSi), 81.00 (CH_2–Si), 113.60 (C_5H_4), 116.89 (C_5H_5), 117.08 (C_5H_4), [C_1(C_5H_4), not observed].

3.5. μ-η^5-η^5-Fulvalenebis[dimethyl(η^5-cyclopentadienyl)titanium(IV)] [{Ti(η^5-C_5H_5)($CH_3)_2\}_2(\mu$-η^5-η^5-$C_{10}H_8$)] (7)

To a suspension of 1.59 g (3.22 mmol) of [{Ti(η^5-C_5H_5)$Cl_2\}_2$(μ-η^5-η^5-$C_{10}H_8$)] in 100 ml of toluene, a solution of 4.3 ml (13 mmol) of MeMgCl in THF was added at −20°C. The reaction mixture was warmed to room temperature and stirred over 12 h. After filtration, the resulting solution was concentrated to 30 ml and cooled at −78°C overnight to give compound **7** as a red-brown crystalline solid. The compound was recrystallized from toluene/hexane (1 g, 75% yield).

Anal. Calc. for $C_{24}H_{30}Ti_2$ (found): C, 69.63 (69.48); H, 7.30 (7.13) %. ^{1}H NMR spectrum (300 MHz, C_6D_6, 25°C): δ 5.91 (t, 4H, C_5H_4), 5.76 (s, 10H, C_5H_5), 5.50 (t, 4H, C_5H_4), 0.14 (s, 12H, CH_3–Ti). The ^{13}C NMR spectrum was not recorded due to its slight solubility.

3.6. μ-η^5-η^5-Fulvalenebis[{bis(trimethylsilylmethyl)}-(η^5-cyclopentadienyl)zirconium(IV)] [{Zr(η^5-C_5H_5)($CH_2SiMe_3)_2\}_2(\mu$-η^5-η^5-$C_{10}H_8$)] (8)

To a suspension of 1.82 g (3.13 mmol) of [{Zr(η^5-C_5H_5)$Cl_2\}_2$(μ-η^5-η^5-$C_{10}H_8$)] in 100 ml of toluene a solution of 1.20 g (12.83 mmol) of $LiCH_2SiMe_3$ in 20 ml of toluene was added at −20°C. The reaction mixture was warmed to room temperature. After 12 h of stirring the solution was filtered and the solvent was removed under vacuum to give a white residue. After extraction with hexane and cooling to −30°C compound **8** was obtained as white crystalline needles. The compound was recrystallized from toluene/hexane (1 g; 52% yield).

Anal. Calc. for $C_{36}H_{62}Si_4Zr_2$ (found): C, 54.72 (54.55); H, 7.91 (8.12) %. ^{1}H NMR spectrum (300 MHz, C_6D_6, 25°C): δ −0.09 (d, $J = 10.01$ Hz, 2H, CH_2–Si), 0.21 (s, 36H, MeSi), 0.38 (d, $J = 10.2$ Hz, 2H, CH_2–Si), 5.40 (t, 4H, C_5H_4), 5.86 (s, 10H, C_5H_4), 6.55 (t, 4H, C_5H_4). ^{13}C NMR spectrum (75 MHz, C_6D_6, 25°C) δ: 3.83 (s, MeSi), 45.8 (s, CH_2–Si), 109.24 (s, C_5H_4), 109.9 (s, C_5H_4), 106.7 (s, C_5H_5), [C_1(C_5H_4), not observed].

3.7. Crystal structure of [{Ti(η^5-C_5H_5)Cl}$_2$(μ-O)(μ-η^5-η^5-$C_{10}H_8$)] (5)

3.7.1. Crystal data

$C_{20}H_{18}Cl_2Ti_2 \cdot 0.5C_7H_7$, $M_r = 487.14$. Monoclinic, space group $C2/c$, $a = 15.033(8)$, $b = 12.122(4)$, $c = 14.008(8)$ Å, $\beta = 109.64(2)°$, $U = 2404(2)$ A^3, $D_c = 1.346$ g cm^{-3}, $Z = 4$; $F(000) = 1096$, $\lambda = 071069$ A, μ(Mo Kα) = 2.50 cm^{-1}.

3.7.2. Data collection and structure solution

A red needle-shaped crystal, under argon in a capillary of approximate size 0.5 × 0.1 × 0.1 mm was mounted on an Enraf–Nonius CAD4 diffractometer, and the intensities of 2453 reflections in the range $1 < \Theta < 24°$ were measured using Mo Kα radiation with a graphite monochromator. The data were corrected for decay and absorption, and reduced to give 1679 reflections (converging at $R = 1.45\%$), of which 1362 had $|F_{obs}| > 6\sigma|F_{obs}|$ and were used in structure solution and refinement. The structure was solved by direct methods (SHELXS) and refined by full-matrix least squares to a conventional R factor of 5.88%. Unit weights were used with hydrogen atoms in calculated positions. All non-hydrogen atoms were given anisotropic temperature factors. A disordered toluene molecule was revealed after the main fragment had been located, and was included in the final refinement with idealised geometry. The final structure is shown in Fig. 1. The atomic coordinates of non-hydrogen atoms are shown in Table 1 and selected bond lengths and angles in Table 2. The remaining data have been deposited in the Cambridge Crystallographic Data Centre. The programs SHELXS and SHELX-76 were used by kind permission of Professor G.M. Sheldrick (University of Gottingen).

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