



ELSEVIER

Dicyclopentadienyl zirconium and hafnium complexes with the bridged (dimethylsilanodiyl)dicyclopentadienyl $[(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2]^{2-}$ ligand. X-ray molecular structure of $[\text{Zr}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}(\text{CH}_2\text{Ph})]_2(\mu\text{-O})$

Tomás Cuenca, Pilar Gómez-Sal, Carlos Martín, Beatriz Royo, Pascual Royo *

Departamento de Química Inorgánica, Edificio Farmacia, Universidad de Alcalá de Henares, Campus Universitario, E-28871 Alcalá de Henares, Spain

Received 31 March 1999

Abstract

Reaction of the bridged (dimethylsilanediyl)dicyclopentadienyl dilithium salt $[(\text{SiMe}_2)(\text{C}_5\text{H}_4)_2\text{Li}_2]$ with MCl_4 , in toluene, gave the zirconium and hafnium complexes $[\text{M}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ [$\text{M} = \text{Zr}$ (1), Hf (2)]. Addition of two equivalents of $\text{M}'\text{R}$ ($\text{M}' = \text{MgCl}$, $\text{R} = \text{CH}_3$; $\text{M}' = \text{Li}$, $\text{R} = \text{CH}_2\text{CMe}_2\text{Ph}$; $\text{M}' = \text{MgBz}$, $\text{R} = \text{CH}_2\text{Ph}$) to toluene or diethyl ether solutions of $[\text{M}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ afforded the dialkyl derivatives $[\text{M}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}\text{R}_2]$ [$\text{R} = \text{CH}_3$, $\text{M} = \text{Zr}$ (3), Hf (4); $\text{R} = \text{CH}_2\text{CMe}_2\text{Ph}$, $\text{M} = \text{Zr}$ (5), Hf (6); $\text{R} = \text{CH}_2\text{Ph}$, $\text{M} = \text{Zr}$ (7)]. Compound 1 reacted with LiMe and $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{THF})_2$ in the presence of a stoichiometric amount of water to give the μ -oxo derivatives $[\text{Zr}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}\text{R}_2(\mu\text{-O})]$ [$\text{R} = \text{CH}_3$ (8), CH_2Ph (9)]. The X-ray molecular structure of $[\text{Zr}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}(\text{CH}_2\text{Ph})]_2(\mu\text{-O})$ (9) has been determined by diffraction methods. Its most remarkable feature is the planarity of the Bz-Zr-O-Zr-Bz and the linearity of the Zr-O-Zr systems. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Hafnium; Silanediyl-cyclopentadienyl; Chloro; Alkyl; Oxoalkyl

1. Introduction

The bis(dimethylsilanediyl)dicyclopentadienyl anion $[\text{SiMe}_2(\text{C}_5\text{H}_4)_2]^{2-}$, synthesized from the corresponding dicyclopentadiene reagent [1], has been successfully used to stabilize Group 4 metal complexes in both high and low oxidation states [2]. This ligand can be coordinated to metal centers as a chelating group to give dicyclopentadienyl *ansa*-metallocene type derivatives [3] or in a bridging disposition to give monocyclopentadienyl or mixed dicyclopentadienyl type complexes [4].

The *ansa*-metallocenes show different reactivity than complexes containing independent cyclopentadienyl rings, and this is of particular interest in reduction reactions [5] or C–H bond activation [6] at these ring

ligands. The presence of two cyclopentadienyl rings linked by a bridging group substantially modifies the mobility of the cyclopentadienyl ligands which subsequently effects the chemical behavior of the compounds.

We are interested in the properties of these *ansa*-derivatives [5,6], and describe herein the synthesis of new chloro-, alkyl- and oxo-alkyl complexes of zirconium and hafnium of the type $[\text{M}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$, $[\text{M}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}\text{R}_2]$ and $[\text{Zr}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}\text{R}_2(\mu\text{-O})]$. The X-ray molecular structure of $[\text{Zr}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}(\text{CH}_2\text{Ph})]_2(\mu\text{-O})$ is also described.

2. Results and discussion

2.1. Preparative results

Reaction of MCl_4 with the lithium reagent $[(\text{SiMe}_2)(\text{C}_5\text{H}_4)_2\text{Li}_2]$ in refluxing toluene gave

* Corresponding author. Tel.: +34-91-8854765; fax: +34-91-8854683.

E-mail address: proyo@inorg.alcala.es (P. Royo)

$[M\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)\}_2\text{Cl}_2]$ [$M = \text{Zr}$ (**1**), Hf (**2**)], containing the *ansa*-(dimethylsilanodiyl)dicyclopentadienyl ligand, isolated as pale-yellow or white microcrystalline solids in high yield.

Compound **1** and its analogous titanium derivative $[\text{Ti}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)\}_2\text{Cl}_2]$ were previously prepared [2a,3a]. Various synthetic routes to prepare analogous compounds have been described [7,8]. The method described in this paper involves some modifications (see Section 3) to the literature methods in order to get purer final products with improved yields.

The reactions of **1** and **2** with alkylating agents have been studied. Treatment of $[M\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)\}_2\text{Cl}_2]$ with $M'R$ ($M' = \text{MgCl}$, $R = \text{CH}_3$; $M' = \text{Li}$, $R = \text{CH}_2\text{CMe}_2\text{Ph}$; $M' = \text{MgBz}$, $R = \text{CH}_2\text{Ph}$) in toluene or diethyl ether and with rigorous exclusion of water gave the dialkyl dicyclopentadienyl derivatives $[M\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)\}_2\text{R}_2]$ [$R = \text{CH}_3$, $M = \text{Zr}$ (**3**), Hf (**4**); $R = \text{CH}_2\text{CMe}_2\text{Ph}$, $M = \text{Zr}$ (**5**), Hf (**6**); $R = \text{CH}_2\text{Ph}$, $M = \text{Zr}$ (**7**)] as white or pale-yellow solids (Scheme 1).

The dialkyl complexes are extremely moisture sensitive. Compound **1** reacts with LiMe and $\text{Mg}(\text{CH}_2\text{Ph})_2$ in the presence of a stoichiometric amount of water to give the μ -oxo dimers $[\text{Zr}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)\}_2\text{R}]_2(\mu\text{-O})$ [$R = \text{CH}_3$ (**8**), CH_2Ph (**9**)] (Scheme 2).

All of the new isolated compounds are soluble in chlorinated solvents (chloroform, dichloromethane) as well as in aromatic hydrocarbons (benzene, toluene) and slightly soluble in hexane and pentane. They can be stored under nitrogen or argon without decomposition.

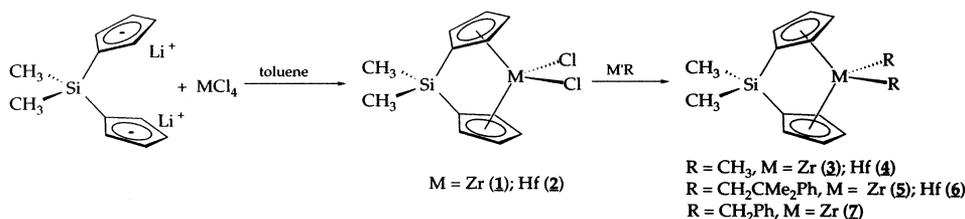
2.2. Structural characterization

The IR spectra of all of these complexes show the characteristic absorptions between 700 and 600 cm^{-1}

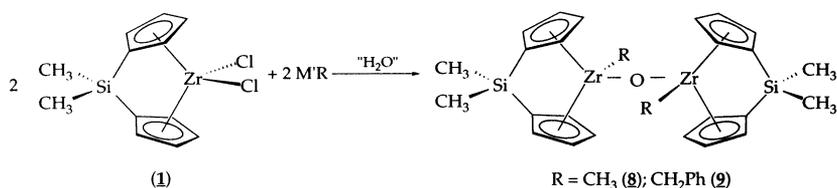
reported [9] for $\nu_{\text{as}}(\text{Si-C})$ and $\nu_{\text{s}}(\text{Si-C})$ vibrations and broad signals near 800 cm^{-1} for the $\nu(\text{M-O-M})$ vibrations in the μ -oxo compounds **8** and **9**.

The ^1H - and ^{13}C -NMR spectra for complexes **1–7** in C_6D_6 show the two pseudotriplets corresponding to an $\text{AA}'\text{BB}'$ spin system typically observed for the protons of the C_5H_4 groups and one singlet for the equivalent methyl groups of the SiMe_2 bridging moiety. These observations are as expected for compounds containing identical groups in the other two pseudotetrahedral positions around the metal center. Likewise, the ^{13}C -NMR data are consistent with this equivalency. In contrast, in compounds **3–7**, the resonances due to the bridgehead carbon atoms are displaced to a higher field than those in the corresponding dichloro precursors, compounds **1** and **2**. This displacement is more pronounced than that observed in analogous compounds containing unsubstituted rings $M(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$. This behavior seems to be characteristic for *ansa*-metallocenes of this type [2a,3a].

The NMR behavior for **8–9** is consistent with that expected for C_s symmetric molecules having equivalent cyclopentadienyl rings, but each showing non-equivalent ring protons and carbon atoms. Therefore their ^1H -NMR spectra show four multiplets for the non-equivalent protons of the ring corresponding to an ABCD spin system and two singlets for the protons of the methyl groups bonded to silicon and located in the equatorial plane of symmetry. Similar behavior is observed in the ^{13}C -NMR spectra, in which five resonances for the ring carbon atoms and two resonances for the methyl groups are observed, data consistent with a chelating dicyclopentadienyl ligand [10].



Scheme 1.



Scheme 2.

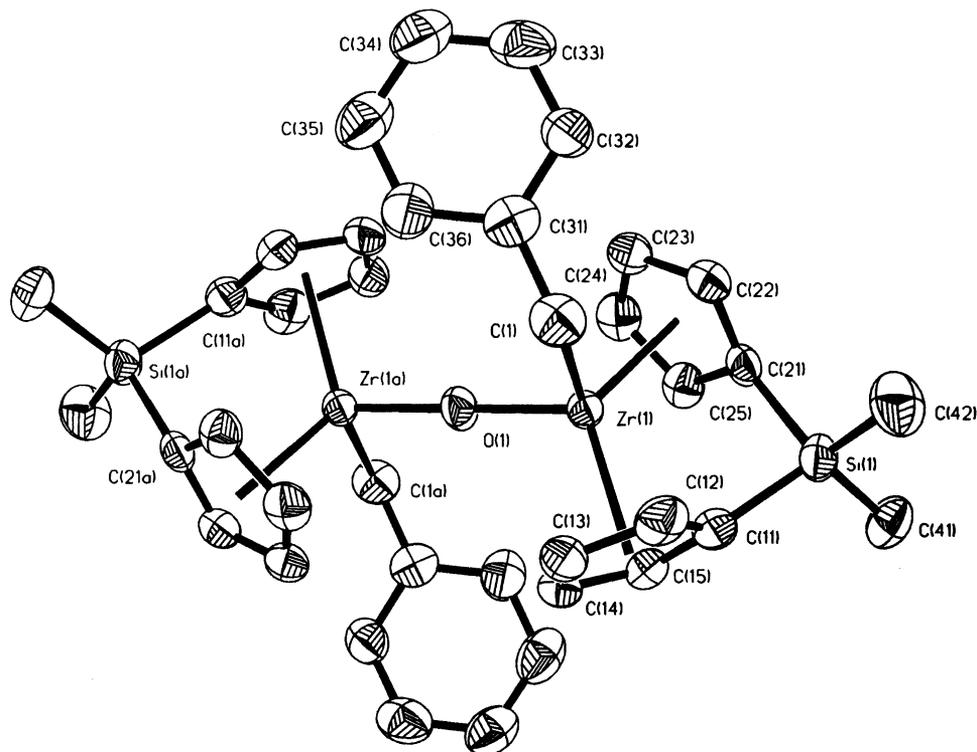


Fig. 1. ORTEP drawing view of the molecular structure of compound **9** together with the atomic labeling scheme.

2.3. Crystal structure of complex $[\text{Zr}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}(\text{CH}_2\text{Ph})]_2(\mu\text{-O})$ (**9**)

The crystal structure of **9** was determined by an X-ray diffraction study. An ORTEP view of the molecular structure with the atomic labeling scheme is shown in Fig. 1. Selected bond angles and distances are given in Table 1.

The molecular structure of **9** shows a dinuclear compound, containing two $[\text{Zr}\{(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)_2\}(\text{CH}_2\text{Ph})$ moieties bound by an oxo-bridging ligand.

Each zirconium center exhibits an *ansa*-metallocene type pseudo-tetrahedral geometry assuming that the ring centroids occupy a single coordination site, comparable to the structures found for ZrCp_2X_2 [11]. Both benzyl groups are located in *trans* positions with respect to the Zr–O–Zr line with the oxygen atom in a symmetric central position and the value of the dihedral angle φ between the two Bz–Zr–O planes is 0° , so that only half of the molecule is present in the asymmetric unit of the unit cell. Since the bridge is highly symmetric, the Zr(1)–O–Zr(1a) angle of 180.0° is disposed in a completely linear fashion. Both Zr–O bond distances are equal (1.9434(5) Å) and shorter than the distance for single Zr–O bonds (average value 2.15–2.20 Å) [11]. This shortening is indicative of a degree of multiple-bonding and is commonly observed in structures of the type $[\text{ZrCp}_2\text{X}]_2(\mu\text{-O})$ [10,12,13]. This is an unusual structural disposition among the $[\text{ZrCp}_2\text{X}]_2(\mu\text{-O})$

derivatives for which stable compounds exhibiting coplanar X–Zr–O–Zr–X and linear Zr–O–Zr conformations are rare.

Checking in the Cambridge Structural Data Base (using QUEST program) [13], 21 compounds with the $[\text{ZrCp}_2\text{X}]_2(\mu\text{-O})$ stoichiometry have been analyzed and the Zr–O distances ranged from 1.99 to 1.94 with a mean value of 1.96 Å, while the Zr–O–Zr angle values ranged from 127.5 to 180.0° , with a mean value of 156.9° , showing no relationship between the two parameters. For most of these structures the Zr–O–Zr bridge is not linear and the angle φ differs significantly from the ideal value of 90° that would optimize the π bonding between oxygen $p\pi$ and the metal LUMO orbitals [12], ranging from 45 to 75° [10,12,13]. Only a few compounds show a completely planar disposition of the X–Zr–O–Zr–X system and a Zr–O–Zr angle of 180° . One example is the bis(tungsten zirconoxycarbene) $[(\text{CO})_5\text{W}-\text{C}(\text{Ph})\text{O}-\text{Cp}_2\text{Zr}-\text{O}-\text{ZrCp}_2-\text{OC}(\text{Ph})-\text{W}(\text{CO})_5]$ complex [12b], which shows a completely planar σ -framework with a *trans* arrangement of the $(\text{CO})_5\text{W}-\text{C}(\text{Ph})\text{O}$ units and a Zr–O–Zr angle of 180° with Zr–O_{bridge} distances of 1.958(1) Å. A similar disposition has been found in the structure of $[\text{Zr}(\text{Cp}_2\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3))_2(\mu\text{-O})]$ [12c,d], which shows Zr–O distances of 1.973 Å and a Zr–O–Zr angle of 180° . The same was observed for $[\text{Zr}(\text{MeC}_5\text{H}_4)_2(p\text{-CH}_3\text{C}_6\text{H}_4)]_2(\mu\text{-O})$ [12e] in which both *p*-tolyl groups are

also located in *trans* positions with respect to the Zr–O–Zr line, and values of 1.965 Å for the Zr–O bond distances and of 180° for the Zr–O–Zr angle were found.

Different reasons based on π -conjugation between the O–Zr–O–Zr–O fragment [12b] and weak agostic C β –H \cdots Zr interactions or alternatively the presence of

Table 1
Bond lengths (Å) and angles (°) for **9**^a

<i>Bond lengths</i>	
Zr(1)–O(1)	1.9434(5)
Zr(1)–C(1)	2.332(6)
Zr(1)–C(15)	2.494(6)
Zr(1)–C(25)	2.493(6)
Zr(1)–C(11)	2.519(6)
Zr(1)–C(21)	2.520(5)
Zr(1)–C(22)	2.533(6)
Zr(1)–C(12)	2.539(6)
Zr(1)–C(24)	2.581(5)
Zr(1)–C(23)	2.580(5)
Zr(1)–C(14)	2.595(6)
Zr(1)–C(13)	2.598(5)
Si(1)–C(42)	1.841(7)
Si(1)–C(41)	1.840(7)
Si(1)–C(11)	1.864(6)
Si(1)–C(21)	1.872(6)
O(1)–Zr(1) # 1	1.9434(5)
C(11)–C(12)	1.419(9)
C(11)–C(15)	1.440(8)
C(12)–C(13)	1.421(9)
C(13)–C(14)	1.396(10)
C(14)–C(15)	1.394(8)
C(21)–C(22)	1.410(9)
C(21)–C(25)	1.429(8)
C(22)–C(23)	1.427(8)
C(23)–C(24)	1.387(9)
C(24)–C(25)	1.412(8)
C(1)–C(31)	1.465(9)
C(31)–C(36)	1.405(9)
C(31)–C(32)	1.409(9)
C(32)–C(33)	1.356(10)
C(33)–C(34)	1.368(11)
C(34)–C(35)	1.378(11)
C(35)–C(36)	1.382(10)
Zr(1)–Cp(1)	2.248
Zr(1)–Cp(2)	2.240
<i>Bond lengths</i>	
O(1)–Zr(1)–C(1)	98.93(17)
C(42)–Si(1)–C(41)	112.2(4)
C(42)–Si(1)–C(11)	112.1(3)
C(41)–Si(1)–C(11)	111.9(3)
C(42)–Si(1)–C(21)	109.9(3)
C(41)–Si(1)–C(21)	113.7(3)
C(11)–Si(1)–C(21)	96.0(2)
Zr(1) # 1–O(1)–Zr(1)	180.0
Cp(1)–Zr(1)–Cp(2)	123.5
C(1)–Zr(1)–Cp(1)	101.3
C(1)–Zr(1)–Cp(2)	106.0
O(1)–Zr(1)–Cp(1)	112.5
O(1)–Zr(1)–Cp(2)	110.8

^a Cp(1), Cp(2) the centroid of C(11)C(12)C(13)C(14)C(15) and C(21)C(22)C(23)C(24)C(25), respectively.

weak C β –H \cdots O hydrogen bonds [12c,d] have been proposed to explain this unusual structural disposition. However, the steric requirements imposed by the X substituents and the cyclopentadienyl rings could be the best explanation for the unusual behavior observed for complex **9**. A very small dihedral angle φ of 17.4° was also observed in the structure of [Zr(^tBu₂C₅H₃)Me]₂(μ -O)[SiMe₂(C₅H₄)₂] [4b], with Zr–O bond distances of 1.955(2) Å and Zr–O–Zr angle of 171.8(1)°, while the less hindered cyclopentadienyl derivatives [Zr(C₅H₅-Cl)₂(μ -O)] [μ -R(C₅H₄)₂] (R = CH₂, SiMe₂) [10] show a dihedral angle between the O–Zr–Cl planes of ca. 45°.

For complex **9**, the (centroid)–Zr–(centroid) (123.5°), the C(1)–Zr(1)–O(1) [98.9(1)°] angles and the Zr(1)–C(1) [2.332(6) Å] and the Zr–(centroid) (2.248 and 2.240 Å) distances are within the expected range [14]. Small differences in the Zr–C(ring) and the C–C ring distances observed suggest a slight deviation from η^5 coordination in the cyclopentadienyl ligand.

3. Experimental

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a VAC model HE 63P or MBraun model 150 GB II glovebox. Solvents were purified by distillation under argon from an appropriate drying agent (phosphorus pentoxide for dichloromethane, sodium–potassium amalgam for hexane, sodium–benzophenone for diethyl ether and THF and sodium for toluene). ZrCl₄, HfCl₄ (Fluka), LiMe, MgClMe, LiNMe₂ (Aldrich) were obtained commercially. [(SiMe₂)(C₅H₄)₂Li₂] [3a,10], LiCH₂CMe₂Ph [15] and Mg(CH₂Ph)₂(THF)₂ [16] were prepared as described in the literature. NMR spectra were recorded on Varian Unity 300 and Varian Unity 500-Plus spectrometers. ¹H and ¹³C chemical shifts are reported in δ units relative to TMS standard. IR spectra were performed in Nujol mulls on a Perkin–Elmer 883 spectrophotometer. Mass spectra were recorded on a Hewlett–Packard 5890 spectrometer. C and H microanalyses were carried out on a Perkin–Elmer 240B microanalyzer.

3.1. Synthesis of [Zr{(SiMe₂)(η^5 -C₅H₄)₂}Cl₂] (**1**)

A solution of freshly prepared [(SiMe₂)(C₅H₄)₂Li₂] (15.4 g, 77 mmol) in THF (150 ml) was slowly added, at –10°C, to a suspension of 28 g (77.25 mmol) of ZrCl₄(THF)₂ in toluene (300 ml). The reaction mixture was then warmed to room temperature (r.t.) and stirred for 14 h. The solvent was completely removed in vacuo to give a yellow oil, which was repeatedly washed with cold hexane. After extraction by Soxhlet into

dichloromethane (250 ml) a clear yellow solution was obtained. This solution was concentrated to 75 ml and cooled at 0°C to give a pale yellow solid. Recrystallization from toluene–hexane gave a yellow crystalline solid characterized as **1** (13.65 g, 39.2 mmol, 51% yield).

3.2. Synthesis of $[Hf\{(SiMe_2)(\eta^5-C_5H_4)_2\}Cl_2]$ (**2**)

Toluene (100 ml) was added to a mixture of $[(SiMe_2)(C_5H_4)_2Li_2]$ (0.98 g, 4.9 mmol) and hafnium tetrachloride (1.57 g, 4.9 mmol) at r.t. and refluxed for 24 h. The reaction mixture was then allowed to cool down to r.t. The toluene solution was filtered through Celite and the solvent was completely removed in vacuo to give a white crystalline solid. Recrystallization from toluene–hexane at –20°C gave a solid characterized as **2** (1.85 g, 4.25 mmol, 87% yield). Anal. Calc. for $C_{12}H_{14}Cl_2HfSi$: C, 33.08; H, 3.24. Found: C, 33.25; H, 3.28%. 1H -NMR (C_6D_6 , 25°C, 300 MHz): δ 0.09 (s, 6H, SiMe₂); 5.41 (t, J_{H-H} = 2.2 Hz, 4H, C₅H₄); 6.69 (t, J_{H-H} = 2.2 Hz, 4H, C₅H₄). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 25°C, 75 MHz): δ –6.2 (SiMe₂); 111.1, 126.5 (s, C₂–C₅); (C_{ipso} not observed).

3.3. Synthesis of $[Zr\{(SiMe_2)(\eta^5-C_5H_4)_2\}(CH_3)_2]$ (**3**)

A 0.95 ml (2.86 mmol) sample of a chloromethyl magnesium 3 M solution in THF was added, at –78°C, to a solution of $[Zr\{(SiMe_2)(\eta^5-C_5H_4)_2\}Cl_2]$ (**1**) (0.5 g, 1.43 mmol) in hexane (75 ml). The reaction mixture was warmed to r.t. and stirred for 12 h. The solution was filtered through Celite and the solvents were completely removed in vacuo to yield a white solid. Recrystallization from toluene–hexane at –20°C gave a microcrystalline white solid characterized as **3** (0.20 g, 0.65 mmol, 45% yield). Anal. Calc. for $C_{14}H_{20}SiZr$: C, 54.67; H, 6.51. Found: C, 54.80; H, 6.26%. 1H -NMR (C_6D_6 , 25°C, 300 MHz): δ –0.03 (s, 6H, SiMe₂); 0.13 (s, 6H, ZrMe); 5.41 (m, 4H, C₅H₄); 6.68 (m, 4H, C₅H₄). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 25°C, 75 MHz): δ –5.4 (SiMe₂); 20.3 (ZrMe); 101.3 (C_{ipso}); 112.4, 120.9 (s, C₂–C₅).

3.4. Synthesis of $[Hf\{(SiMe_2)(\eta^5-C_5H_4)_2\}(CH_3)_2]$ (**4**)

A 0.32 ml (0.96 mmol) sample of a chloromethyl magnesium 3 M solution in THF was added, at –78°C, to a solution of $[Hf\{(SiMe_2)(\eta^5-C_5H_4)_2\}Cl_2]$ (**2**) (0.21 g, 0.48 mmol) in diethyl ether (50 ml). The reaction mixture was stirred for 2 h at low temperature and after 16 h at r.t. a white precipitate was formed. The solution was filtered through Celite and the solvents were completely removed in vacuo to yield a white solid. Recrystallization from toluene–hexane at –20°C gave a microcrystalline white solid characterized as **4** (0.18 g, 0.45 mmol, 94% yield). Anal. Calc. for

$C_{14}H_{20}HfSi$: C, 42.58; H, 5.11. Found: C, 42.23; H, 5.06%. 1H -NMR (C_6D_6 , 25°C, 300 MHz): δ –0.20 (s, 6H, HfMe); 0.15 (s, 6H, SiMe₂); 5.34 (t, J_{H-H} = 2.2 Hz, 4H, C₅H₄); 6.59 (t, J_{H-H} = 2.2 Hz, 4H, C₅H₄). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 25°C, 75 MHz): δ –5.5 (SiMe₂); 36.3 (HfMe); 111.5, 120.3 (s, C₂–C₅), C_{ipso} not observed.

3.5. Synthesis of

$[Zr\{(SiMe_2)(\eta^5-C_5H_4)_2\}(CH_2CMe_2Ph)_2]$ (**5**)

THF (100 ml) was added to a mixture of $[Zr\{(SiMe_2)(\eta^5-C_5H_4)_2\}Cl_2]$ (**1**) (0.50 g, 1.43 mmol) and $LiCH_2CMe_2Ph$ (0.4 g, 2.86 mmol) at –78°C. The reaction mixture was warmed to r.t. and stirred for 12 h. The solvent was completely removed in vacuo to give a solid, which was extracted with hexane (100 ml) to obtain a yellow solution. This solution was concentrated to 25 ml and cooled at 0°C to give a pale yellow solid. Recrystallization from toluene–hexane gave a yellow crystalline solid characterized as **5** (0.43 g, 0.8 mmol, 56% yield). Anal. Calc. for $C_{32}H_{40}SiZr$: C, 69.30; H, 7.75. Found: C, 69.57; H, 7.43%. 1H -NMR (C_6D_6 , 25°C, 300 MHz): δ 0.15 (s, 6H, SiMe₂); 0.99 (s, 4H, ZrCH₂); 1.39 (s, 12H, CMe₂); 5.31 (m, 4H, C₅H₄); 6.41 (m, 4H, C₅H₄); 7.13 (m, 2H, Ph); 7.25 (m, 4H, Ph); 7.36 (m, 4H, Ph). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 25°C, 75 MHz): δ –5.5 (SiMe₂); 34.8 (CMe₂); 43.9 (CMe₂); 75.4 (ZrCH₂); 101.8 (C_{ipso}); 112.6, 119.4 (s, C₂–C₅); 125.4, 125.9, 153.6 (Ph).

3.6. Synthesis of

$[Hf\{(SiMe_2)(\eta^5-C_5H_4)_2\}(CH_2CMe_2Ph)_2]$ (**6**)

Diethyl ether (60 ml) was added to a mixture of $[Hf\{(SiMe_2)(\eta^5-C_5H_4)_2\}Cl_2]$ (**2**) (0.30 g, 0.70 mmol) and $LiCH_2CMe_2Ph$ (0.19 g, 1.35 mmol) at –78°C. The reaction mixture, which immediately turned cloudy due to the precipitation of LiCl, was stirred for 6 h at r.t. The solution was filtered and the solvent removed in vacuo to give a white solid. Recrystallization from toluene–hexane at –20°C gave a microcrystalline white solid characterized as **6** (0.38 g, 0.60 mmol, 86% yield). Anal. Calc. for $C_{32}H_{40}HfSi$: C, 60.89; H, 6.39. Found: C, 60.83; H, 6.26%. 1H -NMR (C_6D_6 , 25°C, 300 MHz): δ 0.16 (s, 6H, SiMe₂); 0.74 (s, 4H, HfCH₂); 1.40 (s, 12H, CMe₂); 5.22 (t, 4H, C₅H₄); 6.37 (t, 4H, C₅H₄), 7.10–7.35 (m, 10H, Ph).

3.7. Synthesis of $[Zr\{(SiMe_2)(\eta^5-C_5H_4)_2\}(CH_2Ph)_2]$ (**7**)

THF (100 ml) was added to a mixture of $[Zr\{(SiMe_2)(\eta^5-C_5H_4)_2\}Cl_2]$ (**1**) (0.50 g, 1.43 mmol) and $Mg(CH_2Ph)_2(THF)_2$ (0.52 g, 1.44 mmol) at –78°C. The reaction mixture was warmed to r.t. and stirred for 12 h. The solvent was completely removed in vacuo to give a solid, which was extracted with hexane (100 ml)

Table 2

Crystal, experimental data and structure refinement procedures for compound **9**

Formula	C ₃₈ H ₄₂ O ₁ Si ₂ Zr ₂
<i>M_w</i>	753.34
Crystal habit	Prismatic
Color	Yellow
Crystal size (mm)	0.25 × 0.28 × 0.30
Symmetry	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.831(1), 10.573(1), 14.889(1)
β (°)	91.26(1)
<i>V</i> (Å ³)	1704.6(3)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.468
<i>F</i> (000)	772
μ (cm ⁻¹)	7.11
Scan mode	$\omega/2\theta$ 2.36 < θ < 26.97
No. of reflections measured	3902
Independent reflections	3707 [<i>R</i> _{int} = 0.0455]
Reflections observed	2154 [<i>I</i> > 2 σ (<i>I</i>)]
Index ranges	0 < <i>h</i> < 13, 0 < <i>k</i> < 13, -18 < <i>l</i> < 18
Standard reflections	3 every 200 reflections
Refinement method	Full matrix least squares on <i>F</i> ²
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^{a,b}	<i>R</i> ₁ = 0.0524, <i>wR</i> ₂ = 0.1104
Largest difference peak and hole (e Å ⁻³)	2.057, -0.591
Goodness of fit on <i>F</i> ²	1.022

^a *R*₁ = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$; *wR*₂ = $\{\Sigma\omega(F_o^2 - F_c^2)/[\Sigma\omega(F_o^2)]\}^{1/2}$.^b Weighting scheme calc. $w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 1.9522P]$ where $P = (F_o^2 + 2F_c^2)/3$.

to obtain a yellow solution. This solution was concentrated to 25 ml and cooled at 0°C to give a pale yellow solid. Recrystallization from toluene–hexane gave a yellow crystalline solid characterized as **7** (0.30 g, 0.65 mmol, 45% yield). Anal. Calc. for C₂₆H₂₈SiZr: C, 67.93; H, 6.10. Found: C, 67.50; H, 6.15%. ¹H-NMR (C₆D₆, 25°C, 300 MHz): δ -0.06 (s, 6H, SiMe₂); 1.74 (s, 4H, ZrCH₂); 5.13 (m, 4H, C₅H₄); 6.31 (m, 4H, C₅H₄); 6.79 (m, 4H, Ph); 6.84 (m, 2H, Ph); 7.12 (m, 4H, Ph). ¹³C{¹H}-NMR (C₆D₆, 25°C, 75 MHz): δ -6.4 (SiMe₂); 55.8 (ZrCH₂); 100.3 (C_{ipso}); 112.5, 121.4 (s, C₂-C₅); 125.6, 127.8, 149.2 (Ph).

3.8. Synthesis of [Zr{(SiMe₂)(η^5 -C₅H₄)₂}(CH₃)₂](μ -O) (**8**)

1.8 ml (2.88 mmol) of a MeLi 3 M solution in diethyl ether was added, at -78°C, to a solution of [Zr{(SiMe₂)(η^5 -C₅H₄)₂Cl₂] (**1**) (0.50 g, 1.43 mmol) in toluene (75 ml). The reaction mixture was stirred with a stoichiometric amount of water (0.015 ml, 0.72 mmol) for 2 h at low temperature and then for 12 h at r.t. with formation of a white precipitate. The solution was filtered through Celite and the solvents were completely

removed in vacuo to yield a white solid. Recrystallization from toluene–hexane at -20°C gave a microcrystalline white solid characterized as **8** (0.18 g, 0.30 mmol, 42% yield). Anal. Calc. for C₂₆H₃₄OSi₂Zr₂: C, 51.94; H, 5.66. Found: C, 52.17; H, 5.64%. ¹H-NMR (C₆D₆, 25°C, 300 MHz): δ 0.22 (s, 3H, SiMe₂); 0.31 (s, 3H, SiMe₂); 0.42 (s, 3H, ZrMe); 5.51 (m, 2H, C₅H₄); 6.01 (m, 2H, C₅H₄); 6.23 (m, 2H, C₅H₄); 6.54 (m, 2H, C₅H₄). ¹³C{¹H}-NMR (C₆D₆, 25°C, 75 MHz): δ -4.7, -5.8 (SiMe₂); 20.3 (ZrMe); 111.4 (C_{ipso}); 108.6, 114.0, 119.7, 120.7 (C₂-C₅). EI MS (70 V): *m/z* = 585 ([M - CH₃]⁺, 100%).

3.9. Synthesis of

[Zr{(SiMe₂)(η^5 -C₅H₄)₂}(CH₂Ph)]₂(μ -O) (**9**)

A solution of Mg(CH₂Ph)₂(THF)₂ (0.52 g, 1.44 mmol) in THF (50 ml) was added, at -78°C, to a solution of [Zr{(SiMe₂)(η^5 -C₅H₄)₂Cl₂] (**1**) (0.50 g, 1.43 mmol) in toluene (75 ml). The reaction mixture was stirred with a stoichiometric amount of water (0.015 ml, 0.72 mmol) for 2 h at low temperature and for 12 h at r.t. to give a white precipitate. The solution was filtered through Celite and the solvent was completely removed in vacuo to yield a yellow solid. Recrystallization from toluene–hexane at -20°C gave a microcrystalline yellow solid characterized as **9** (0.35 g, 0.46 mmol, 64% yield). Anal. Calc. for C₃₈H₄₂OSi₂Zr₂: C, 60.59; H, 5.58. Found: C, 59.82; H, 5.81%. ¹H-NMR (C₆D₆, 25°C, 300 MHz): δ 0.16 (s, 3H, SiMe₂); 0.42 (s, 3H, SiMe₂); 2.4 (s, 2H, ZrCH₂); 5.57 (m, 2H, C₅H₄); 6.05 (m, 2H, C₅H₄); 6.10 (m, 2H, C₅H₄); 6.22 (m, 2H, C₅H₄); 6.95 (m, 2H, Ph); 7.34 (m, 3H, Ph). ¹³C{¹H}-NMR (C₆D₆, 25°C, 75 MHz): δ -4.0, -6.6 (SiMe₂); 50.3 (ZrCH₂); 111.4 (C_{ipso}); 108.3, 117.1, 117.4, 121.1 (C₂-C₅); 123.6, 126.7, 135.7, 153.1 (Ph).

3.10. Crystal structure determination of complex

[Zr{(SiMe₂)(η^5 -C₅H₄)₂}(CH₂Ph)]₂(μ -O) (**9**)

A suitable sized yellow crystal of compound **9** was obtained by crystallization from toluene–hexane at -30°C and mounted in a Lindemann capillary on an Enraf–Nonius CAD 4 automatic four-circle diffractometer with bisecting geometry equipped with a graphite monochromated Mo–K α radiation (λ = 0.71073 Å). Crystallographic and experimental details of the crystal structure determination are summarized in Table 2. Data were collected at r.t. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by direct methods (SHELXL-90) [17] and refined by least-squares against *F*² (SHELXL-93) [18]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were intro-

duced from geometrical calculations and refined using a riding model with fixed thermal parameters. Calculations were carried out on an ALPHA AXP (Digital) workstation.

4. Supplementary material

Crystallographic data, including tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters for the non-hydrogen atoms and a complete list of bond distances and angles, for compound **9** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CSD-116494. Ordering information is given on any current masthead page.

Acknowledgements

We acknowledge the Dirección General de Investigación Científica y Técnica (Spain) for financial support of this research (Project PB97-0776).

References

- [1] K.C. Frisch, *J. Am. Chem. Soc.* 75 (1953) 6050.
- [2] (a) H. Yasuda, N. Nagasuna, M. Akita, K. Lee, A. Nakamura, *Organometallics* 3 (1984) 1470. (b) R. Gómez, T. Cuenca, P. Royo, W.A. Herrmann, E. Herdtweck, *J. Organomet. Chem.* 382 (1990) 103. (c) R. Gómez, T. Cuenca, P. Royo, E. Hovestreydt, *Organometallics* 10 (1991) 2516 and Refs. cited therein.
- [3] (a) J.A. Smith, J. von Seyerl, G. Huttner, H.H. Brintzinger, *J. Organomet. Chem.* 173 (1979) 175. (b) H. Wiesenfeldt, A. Reinmuth, E. Barstiers, K. Evertz, H.H. Brintzinger, *J. Organomet. Chem.* 369 (1989) 359. (c) C.S. Bajgur, W.R. Tikkanen, J.L. Petersen, *Inorg. Chem.* 24 (1985) 2539. (d) T. Mise, S. Miya, H. Yamazaki, *Chem. Lett.* (1989) 1853 (e) X.-Z. Zhou, Y. Wang, S.-S. Xu, H.-G. Wang, X.-K. Yao, *Chem. Res. Chin. Univ.* 28 (1992) 239. (f) A. Razavi, J.L. Atwood, *J. Organomet. Chem.* 497 (1995) 105. (g) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143.
- [4] (a) S. Ciruelos, T. Cuenca, P. Gómez-Sal, A. Martín, P. Royo, *Organometallics* 12 (1993) 944. (b) G. Ciruelo, T. Cuenca, P. Gómez-Sal, A. Martín, P. Royo, *J. Chem. Soc. Dalton Trans.* (1995) 231. (c) T. Cuenca, J.C. Flores, R. Gómez, P. Gómez-Sal, M. Parra-Hake, P. Royo, *Inorg. Chem.* 32 (1993) 3606.
- [5] (a) R. Gómez, T. Cuenca, P. Royo, M.A. Pellinghelli, A. Tiripicchio, *Organometallics* 10 (1991) 1505. (b) T. Cuenca, R. Gómez, P. Gómez-Sal, P. Royo, *J. Organomet. Chem.* 454 (1993) 105. (c) T. Cuenca, A. Padilla, P. Royo, M. Parra-Hake, M.A. Pellinghelli, A. Tiripicchio, *Organometallics* 14 (1994) 848.
- [6] R.M. Shaltout, J.Y. Corey, N.P. Rath, *J. Organomet. Chem.* 503 (1995) 205.
- [7] (a) G. Chandra, M.F. Lappert, *J. Chem. Soc. (A)* (1968) 1940. (b) H. Köpf, W. Kahl, *J. Organomet. Chem.* 64 (1974) C37. (c) A.K. Hughes, A. Meetsma, J. Teuben, *Organometallics* 12 (1993) 1936.
- [8] (a) W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1946. (b) D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, *Organometallics* 15 (1996) 1572.
- [9] K. Nakamoto, in: M. Tsutsui (Ed.), *Characterization of Organometallic Compounds*, Wiley-Interscience, New York, 1969.
- [10] K.P. Reddy, J.L. Petersen, *Organometallics* 8 (1989) 2107.
- [11] D.J. Cardin, M.F. Lappert, C.L. Raston, *Chemistry of Organozirconium and Hafnium Compounds*, Ellis Horwood, London, 1986.
- [12] (a) J.L. Petersen, *J. Organomet. Chem.* 166 (1979) 179. (b) G. Erker, U. Dorf, C. Krüger, Y.H. Tsay, *Organometallics* 6 (1987) 680. (c) U. Rosenthal, A. Ohff, M. Michalick, H. Görls, V.V. Burlakov, V.B. Shur, *Organometallics* 12 (1993) 5016. (d) R. Kempe, A. Ohff, U. Rosenthal, *Z. Kristallogr.* 211 (1996) 495. (e) W. Zutao, C. Shoushan, Y. Xinkan, D. Yicheng, W. Shen, Z. Jiping, W. Anzhi, Z. Rongguang, *Sci. Sin. Ser. B (Eng. Ed.)* 25 (1982) 1133.
- [13] F.H. Allen, O. Kennard, *Chemical Design Automation News* 8 (1) (1993) 31.
- [14] (a) K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton, G.V. Rees, *Acta Crystallogr. Sect. B* 30 (1974) 2290. (b) E.L. Lyszak, J.P. O'Brien, D.A. Kort, S.K. Hendges, R.N. Redding, T.L. Busch, M.S. Hermen, K.B. Renkema, M.E. Silver, J.C. Huffman, *Organometallics* 12 (1993) 338.
- [15] C. Tessiers, O.T. Beachley, *Inorg. Synth.* 24 (1986) 95.
- [16] R.R. Schrock, *J. Organomet. Chem.* 122 (1976) 209.
- [17] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 46 (1990) 467.
- [18] G.M. Sheldrick, *SHELXL-93*, University of Göttingen, Germany, 1993.